An assessment of the ability of three-dimensional air quality models with current thermodynamic equilibrium models to predict aerosol NO$_3^-$

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[1]   The partitioning of total nitrate (TNO$_3$) and total ammonium (TNH$_4$) between gas and aerosol phases is studied with two thermodynamic equilibrium models, ISORROPIA and the aerosol inorganics model (AIM), and three data sets: high time resolution measurement data from the 1999 Atlanta Supersite Experiment (summer case) and the 2002 Pittsburgh Air Quality Study (PAQS) Supersite Experiment (winter case), and 12-hour measurement data from the Clinton site, North Carolina, in 1999. At the Atlanta site, both models reproduced a large percentage of the observed aerosol NH$_4^+$ and HNO$_3$ (NH$_4^+$: >94% and HNO$_3$: >86%) within a factor of 1.5, whereas neither model reproduced a majority of observed aerosol NO$_3^-$ and NH$_3$ (NO$_3^-$: <48% and NH$_3$: <51%) within a factor of 2. At the Pittsburgh site, both models reproduced more than 76% of observed NO$_3^-$ within a factor of 2. At the Clinton site, both models performed a little better on aerosol NO$_3^-$ (47–58% within a factor of 1.5) than at the Atlanta site but worse than at the Pittsburgh site. Sensitivity test of thermodynamic models with Gaussian random errors indicates that in many cases, measurement errors in SO$_4^{2-}$ and TNH$_4$ can explain a major fraction of the discrepancies between the equilibrium model predictions and observations in partitioning of TNO$_3$. Comparison of predictions of the three-dimensional (3-D) Community Multiscale Air Quality (CMAQ) model with the observations over the continental United States indicates that the performance of the 3-D model for NO$_3^-$, HNO$_3$, NH$_4^+$, and NH$_3$ strongly depends on its performance for TNO$_3$, TNH$_4$, and SO$_4^{2-}$. Tests show that errors associated with SO$_4^{2-}$ and TNH$_4$ predictions of the 3-D model can result in the thermodynamic model calculation replicating only 47% and 60% of base case NO$_3^-$ within a factor of 2 for summer and winter cases, respectively. It was found that errors in TNH$_4$ are more critical than errors in SO$_4^{2-}$ to prediction of NO$_3^-$.

1.   Introduction

[2]   Atmospheric fine particles are predominately composed of sulfate, nitrate, ammonium, sodium, chloride, water, organic species and trace metals [*Russell and Cass*, 1984; *Malm et al.*, 1994; *Environmental Protection Agency* (*EPA*), 1996, 1998; *Yu et al.*, 2003]. Fine particles refer to the particles with diameters less than 2.5 μm (PM$_{2.5}$). The inorganic species of sulfate, nitrate and ammonium constitute a major fraction of atmospheric aerosols. The behavior of nitrate is one of the most intriguing aspects of inorganic atmospheric aerosols because particulate nitrate concentrations depend not only on the amount of nitric acid, but also on the availability of ammonia and sulfate, together with temperature and relative humidity. Particulate nitrate is produced predominantly from the equilibrium reaction between two gas-phase species, HNO$_3$ and NH$_3$. Generally, ammonia reacts preferentially with acidic sulfate particles

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(H_2SO_4 or HSO_4^-) and if sufficient ammonia remains, it can react with HNO_3 to form particulate NH_4NO_3. Over the eastern United States, nitrate concentrations in the summer are low since sulfate levels are high, temperatures are elevated and available ammonia is limited (NH_3 limitation). Winter nitrate concentrations are higher because sulfate levels are lower, temperatures are lower and more ammonia is available [*EPA*, 1996, 1998; *Blanchard and Hidy*, 2003]. Over the western United States, especially in California where higher NH_3 and lower SO_2 emissions allow complete neutralization of H_2SO_4, formation of aerosol nitrate depends upon the availability of nitric acid (HNO_3 limitation) and nitrate concentrations are higher than sulfate in both summer and winter. These interactions are dynamic and changes of H_2SO_4 due to changes of SO_2 emissions can leave more or less NH_3 to react with HNO_3 and lead to changes in nitrate concentration. Predictions of particulate matter concentrations by 3-D air quality models need to consider the full range of interactions in both eastern and western United States, creating a major challenge for the models. The interactions are simulated with thermodynamic equilibrium models incorporated into the 3-D air quality models.

[3] Several inorganic thermodynamic models have been developed during the past two decades to partition the semivolatile species between gas and aerosol phases. These include EQUIL [*Basset and Seinfeld*, 1983], MARS [*Saxena et al.*, 1986], EQUILIB [*Pilinis and Seinfeld*, 1987], AIM [*Wexler and Seinfeld*, 1990; *Clegg et al.*, 1998; *Wexler and Clegg*, 2002], SCAPE [*Kim et al.*, 1993], EQUISOLV [*Jacobson et al.*, 1996] and ISORROPIA [*Nenes et al.*, 1999], each with their own strengths and weakness [*Zhang et al.*, 2000]. The comparative review of *Zhang et al.* [2000] showed that the particulate matter (PM) composition and concentrations predicted by five modules (i.e., MARS-A, SEQUILIB, SCAPE2, EQUISOLV II and AIM2) were generally comparable under most conditions. Significant discrepancies existed under some conditions, however, especially at high nitrate/chloride concentrations and low/medium relative humidity (RH) [*Zhang et al.*, 2000]. It has been postulated and confirmed by ambient measurements that the fine-particle sulfate/nitrate/ammonium aerosol constituents should be in thermodynamic equilibrium with the local gas phase, consistent with the calculations of the thermodynamic equilibrium models [*Stelson and Seinfeld*, 1982; *Basset and Seinfeld*, 1983; *Saxena et al.*, 1986; *Wexler and Seinfeld*, 1990; *Nenes et al.*, 1999; *Ansari and Pandis*, 2000; *Moya et al.*, 2001]. However, if coarse particles are involved in interactions of the inorganic system, nonequilibrium conditions between the bulk gas phase and particles can exist because the equilibrium timescale of these interactions can be long, on the order of hours instead of seconds [*Allen et al.*, 1989; *Wexler and Seinfeld*, 1990; *Meng and Seinfeld*, 1996]. For example, *Moya et al.* [2001] found that a dynamic approach instead of an equilibrium approach was more capable of reproducing aerosol nitrate behavior under high temperature (>20°C) and low RH (<40%) conditions observed during a field experiment in Mexico City. The equilibrium models also assume internal mixtures of aerosols. A study of the nitrate partitioning with the GFEMN chemical equilibrium model at Pittsburgh [*Takahama et al.*, 2004] showed that during

periods in July with low relative humidity, simulating the particles as an external mixture of crystallized ammonium sulfate and wet, acidic particles could significantly improve agreement between predictions and measurements. Nonetheless, Monte Carlo simulations with GFEMN also indicated that in general one could expect reasonable agreement between predictions of a chemical equilibrium model and measurements.

[4] It is a very challenging task to partition the semivolatile inorganic aerosol components between the gas and aerosol phases correctly. The normalized mean error (NME) for predictions of nitrate is typically three times that for predictions of sulfate for a variety of 3-D air quality models applied to sections of the United States [*Odman et al.*, 2002; *Pun et al.*, 2004; *Seigneur and Moran*, 2004]. For an annual average across the entire United States the NMEs of the predictions of nitrate from the U.S. EPA Models-3/Community Multiscale Air Quality Model (CMAQ) are from two to three times larger than the NMEs for sulfate, depending on which continental network the model is being compared to, while the NMEs for PM2.5 are only 10–20% larger than those for sulfate. The objectives of this work are: (1) to evaluate the performance of two standalone thermodynamic models (AIM2 [*Clegg et al.*, 1998; *Wexler and Clegg*, 2002] and ISORROPIA [*Nenes et al.*, 1999]) by comparing the predicted partitioning of total nitrate (gas plus aerosol) and total ammonia (gas plus aerosol) between gas and aerosol phases with that of observations using high time-resolution measurement data obtained during the 1999 Atlanta Supersite Experiment [*Weber et al.*, 2003] and the 2002 Pittsburgh Air Quality Study (PAQS) Supersite Experiment [*Wittig et al.*, 2004], and using 12-hour measurement data taken at the Clinton site, NC, in 1999 [*Robarge et al.*, 2002]; and (2) to assess the skill inherent in a current 3-D air quality model at predicting aerosol nitrate concentrations based on partitioning with the ISORROPIA thermodynamic model used as a module. ISORROPIA has been designed to be used in 3-D air quality models and is incorporated in the U.S. EPA Models-3/CMAQ model. We focus on the partitioning of total nitrate, because it is one of the most important semivolatile aerosol species, but results regarding the partitioning of total ammonium are also discussed.

2. Description of Thermodynamic Equilibrium Models and Observational Data Sets

2.1. Thermodynamic Models

[5] Given total (gas plus fine particulate phase) concentrations of H_2SO_4, HNO_3, and NH_3, and temperature and RH as inputs, ISORROPIA [*Nenes et al.*, 1999] and AIM (AIM model II is used in this study) [*Clegg et al.*, 1998; *Wexler and Clegg*, 2002] predict the partitioning of these inorganic species between the gas and fine particle (PM$_{2.5}$) phases on the basis of thermodynamic equilibrium. Most of the total H_2SO_4 is in the aerosol phase because it has a very low vapor pressure and its gas-phase concentration is considered negligible [*Seinfeld and Pandis*, 1998]. Although ISORROPIA and AIM also allow the inclusion of sea salt species (Na^+ and Cl^-) into their modeling frameworks, this study will focus on thermodynamic equilibrium for the sulfate/nitrate/ammonium system. In this

study, aerosol NH_4^+ plus gas NH_3 and aerosol NO_3^- plus gas HNO_3 are referred to as TNH_4 and TNO_3, respectively. The aerosol particles are assumed to be internally mixed, i.e., all particles of the same size have the same chemical composition, and in bulk thermodynamic equilibrium with the gas phase with no size resolution. The metastable equilibrium state (efflorescence behavior) is assumed in all thermodynamic equilibrium calculations in this study, i.e., aerosol particles are liquid at all times. More detailed descriptions of the equilibrium reactions and the solution procedures for AIM and ISORROPIA are given by *Wexler and Clegg* [2002] and *Nenes et al.* [1999], respectively. *Zhang et al.* [2000] reviewed the similarities, differences and their likely causes of five different thermodynamic models. The differences between ISORROPIA and AIM are briefly summarized here. ISORROPIA uses the Kusik-Messner method to calculate the multicomponent activity coefficients and the Zdanovskii, Robinson and Stokes (ZSR) method to calculate water activity, whereas AIM uses the Pitzer, Simonson and Clegg method for multicomponent activity coefficients and mole fraction based electrolyte thermodynamic models for water activities. In ISORROPIA the equilibrium state of the gas/aerosol system is calculated from equality of chemical potentials using Newton-Raphson and bisectional method, whereas in AIM by direct minimization of the Gibbs Free Energy and without applying any simplifying assumptions for the inorganic aerosol system. ISORROPIA utilizes the optimal solution of the thermodynamic equations and pre-calculated tables, whenever possible [*Nenes et al.*, 1999], to render the thermodynamic model as fast and computationally efficient as possible. ISORROPIA is suitable for incorporation into 3-D air quality models due to its computational efficiency. AIM is a theoretically complete and accurate phase equilibrium model. The AIM model II is extended to include the dissociation of water and of aqueous NH_4^+ so that the model can be used for phase equilibrium calculations for neutral and/or slightly alkaline aerosols [*Clegg et al.*, 1998; *Wexler and Clegg*, 2002]. In this extension the activity coefficient of aqueous OH^- is assumed to follow the Debye-Huckel limiting law, and all model interaction parameters involving aqueous NH_3 were set to zero. AIM [*Clegg et al.*, 1998] is one of the few thermodynamic models able to simulate the behavior of double salts other than letocivite, $(NH_4)_3H(SO_4)_2$. AIM is suitable for the analysis of experimental data, but it is very slow and is not currently configured for incorporation into 3-D air quality models. It should be remembered that there are some limitations of using these thermodynamic models in analyzing the observations because of the uncertainties of equilibrium constants and activity coefficients obtained by laboratory experiments and model calculations. Some other limitations of thermodynamic models will be discussed in section 3.1.2

2.2. Observational Data Sets

[6] Three sites were chosen that had higher time resolution data to better test the equilibrium models. They were the Atlanta, Georgia Supersite (summer), the Pittsburgh, Pennsylvania Supersite (winter) and the Clinton Horticultural Station in North Carolina (all year). The different chemical and meteorological conditions at the three sites could be used to help interpret equilibrium model perform-

ances in partitioning TNO_3 and TNH_4. As analyzed below, for example, the Atlanta site had very high SO_4^{2-} concentrations and high temperatures and relatively high molar ratios of TNH_4 to SO_4^{2-} (3.77), the Pittsburgh site had low temperatures and very high TNH_4 concentrations (molar ratio of TNH_4 to SO_4^{2-} of 9.22) and the Clinton site had high relative humidity.

[7] At the Atlanta site (33.78°N, 84.41°W) during the SOS/Atlanta '99 Supersite Experiment from 18 August to 1 September 1999, the concentrations of $PM_{2.5}$ SO_4^{2-}, NO_3^-, and NH_4^+ were measured by the Particle Into Liquid Sampler with a 5-min sampling and a 7-min duty cycle [*Weber et al.*, 2003]. NH_3 (g) concentrations were measured by the ECN SJAC-Aerosol Sampler with a time resolution of 15 min [*Slanina et al.*, 2001], while the HNO_3 (g) concentrations were determined by the ARA instrument with a time resolution of 9 min [*Edgerton et al.*, 2000]. These 9-min HNO_3 and 15-min NH_3 concentrations were parsed into 5-min averages so as to overlap with 5-min mean concentrations of $PM_{2.5}$ SO_4^{2-}, NO_3^-, and NH_4^+. Temperature and RH with 1-min time resolution were determined by two independently operated sets of meteorological equipment [*Edgerton et al.*, 2000]. The 5-min averages of temperature and RH from the two sets of observations were used in this study. A total of 325 data points at the Atlanta site were obtained in this way.

[8] At the Pittsburgh Supersite (40.44°N, 79.94°W), Pennsylvania, the concentrations of $PM_{2.5}$ SO_4^{2-} and NO_3^- were measured by the Ruprecht and Patashnik sampling system (R&P sampler) with a time resolution of 1 hour, and concentrations of TNO_3 and TNH_4 were determined by a steam sampler with a time resolution of 2 hours [*Wittig et al.*, 2004]. The 2-hour mean concentrations of $PM_{2.5}$ SO_4^{2-} and NO_3^- were calculated by the simple averaging of their corresponding 1-hour measurements and used with the 2-hour mean concentrations of TNO_3 and TNH_4. Two-hour mean HNO_3 concentrations were estimated by subtracting $PM_{2.5}$ NO_3^- concentrations from TNO_3. Temperature and RH were determined by Campell HMP45C thermistor-based sensor and capacitance thin film sensor, respectively. A total of 313 data points at the Pittsburgh site were obtained during the period of 2–31 January 2002.

[9] At the Clinton Horticultural Crop Research Station (35°01′N, 78°16′W), North Carolina, 12-hour (0600–1800 EST day cycle; 1800–0600 EST night cycle) mean concentrations of $PM_{2.5}$ NH_4^+, NO_3^- and SO_4^{2-}, and gas NH_3 and HNO_3 were measured by an annular denuder system from 20 January to 2 November 1999 [*Robarge et al.*, 2002]. Standard hourly temperature and RH data at the Clinton site were measured by the State Climate Office of North Carolina at North Carolina State University.

3. Results and Discussion

3.1. Test of Thermodynamic Models With Observational Data

3.1.1. Results at Atlanta, Pittsburgh, and Clinton Sites

[10] Measured concentrations of SO_4^{2-}, TNH_4 and TNO_3, and temperature and RH are input to ISORROPIA and AIM. The partitioning of TNH_4 and TNO_3 between the gas and aerosol phases is then predicted by the models. Comparisons of observed aerosol NO_3^- and NH_4^+, and gaseous
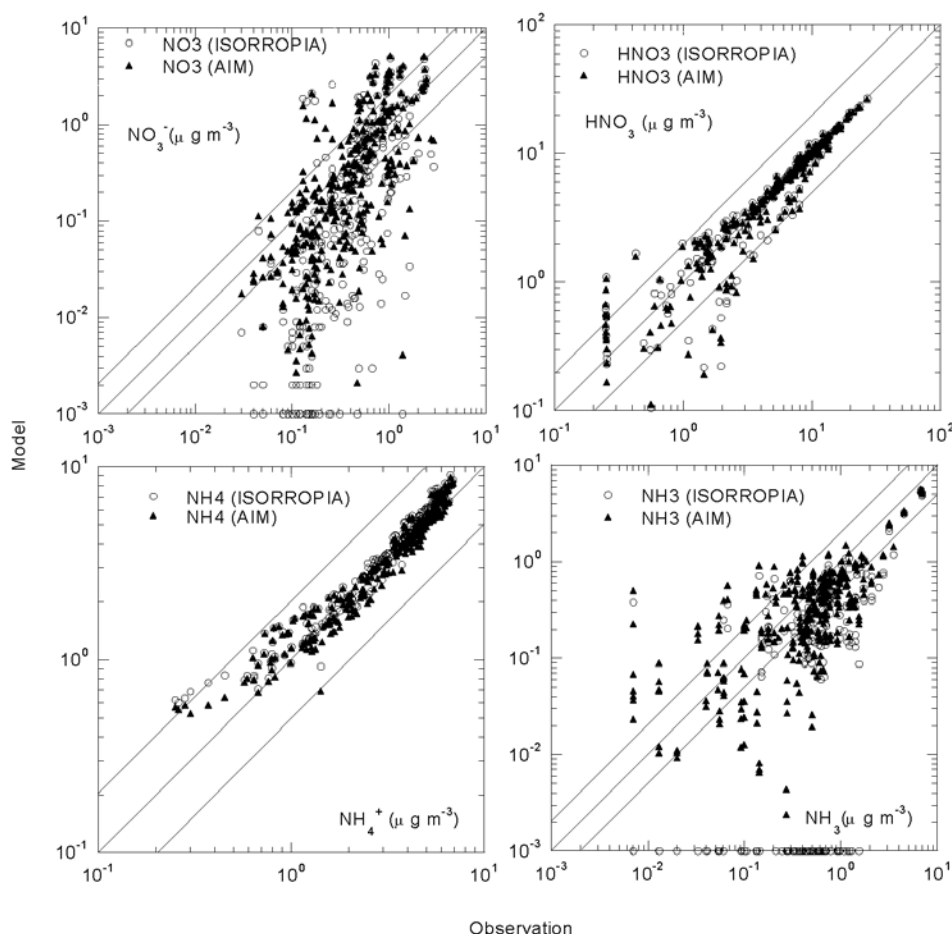
Figure 1. Comparison of the modeled (ISORROPIA and AIM) partitioning of total nitrate (gas plus aerosol) and total ammonia (gas plus aerosol) between gas and aerosol phases with that of observations for aerosol NO_3^-, HNO_3, aerosol NH_4^+, and NH_3 at the Atlanta Supersite in summer of 1999. Note that points with $<10^{-3}$ are made equal to 10^{-3}. The 1:1, 2:1, and 1:2 lines are shown for reference.

HNO_3 and NH_3 concentrations with those calculated by ISORROPIA and AIM at the Atlanta site are shown in Figure 1 and Table 1. The partitioning of TNO_3 and TNH_4 between gas and aerosol phases by ISORROPIA and AIM is similar. The percentage of predictions agreeing within a factor of 1.5 or 2 of the observations is slightly higher for AIM than for ISORROPIA for each species. AIM predicts slightly more NO_3^- and NH_3 but less HNO_3 and NH_4^+ compared to ISORROPIA although the differences between the two models are not significant. When one phase is dominant, small relative errors in predictions of the species in the dominant phase lead to large relative errors for the other phase, since the total concentrations of the prediction and the observation are the same. For example, 94.8% and 96.0% of the ISORROPIA and AIM predictions of NH_4^+ are within a factor of 1.5 of the observations. ISORROPIA and AIM also predict HNO_3 well, with 86% and 87% of the predictions within a factor of 1.5 of the observations. However, both equilibrium models are unable to replicate a majority of the observed NO_3^- and NH_3 concentrations, see Figure 1 and Table 1. For NO_3^-, only 32% and 48% of the ISORROPIA and AIM predictions are within a factor of 2 of the observations, respectively. For NH_3, ISORROPIA

and AIM replicate 25.2% and 51.4% of the observations within a factor of 2, respectively. As will be shown below, one of the reasons for this behavior is that NO_3^- and NH_3 concentrations at the Atlanta site are very low and very sensitive to any errors in SO_4^{2-} and TNH_4.

[11] The results at the Pittsburgh site are very different from those at the Atlanta site as shown in Figures 2 and 3 and Table 1. The mean observed aerosol NO_3^- concentration (2.09 $\mu g\ m^{-3}$) at the Pittsburgh site is about 4 times higher than that at the Atlanta site (0.53 $\mu g\ m^{-3}$), whereas the observed mean TNO_3 concentration at Pittsburgh (3.09 $\mu g\ m^{-3}$) is only half of that at the Atlanta site (7.56 $\mu g\ m^{-3}$) (see Table 1). The mean SO_4^{2-} and TNH_4 concentrations at the Pittsburgh site are 2.46 and 1.76 $\mu g\ m^{-3}$ respectively, much lower than those at the Atlanta site (12.17 and 4.38 $\mu g\ m^{-3}$ for SO_4^{2-} and TNH_4, respectively). The relatively high molar ratios of TNH_4 to SO_4^{2-} for most cases (mean: 3.77, i.e., sulfate-poor conditions) and low temperatures (3.9 ± 5.9°C) at the Pittsburgh site result in a higher percentage of TNO_3 partitioning into aerosol NO_3^- (68%) when compared to that at the Atlanta site (7%), where the mean molar ratio of TNH_4 to SO_4^{2-} is 1.92 and temperature is 25.0 ± 3.3 °C (see Table 1). Because the TNO_3

Table 1. Statistical Summaries of the Comparison of the Modeled (ISORROPIA and AIM2) Partitioning of Total Nitrate (Gas Plus Aerosol) and Total Ammonia (Gas Plus Aerosol) Between Gas and Aerosol Phases With That of Observations at the Atlanta Supersite, GA, Pittsburgh Supersite, PA, and Clinton Site, NC, and the Mean Concentrations of SO_4^{2-} ($\mu g\ m^{-3}$), TNH_4 ($\mu g\ m^{-3}$), and Relative Humidity (RH) (%) and Temperature (T) ($^{\circ}$C) at Each Site Are Also Listed (The Value is "Mean ± Standard Deviation")

Parameters	$\langle C \rangle^a$			Percent Within a Factor of 1.5^b		Percent Within a Factor of 2^b	
	Observation	ISORROPIA	AIM	ISORROPIA	AIM	ISORROPIA	AIM
			At Atlanta Site (N = 325)^c				
Aerosol NO_3^-	0.53 ± 0.51	0.54 ± 0.92	0.61 ± 0.92	21.8	33.2	31.7	48.3
Gas HNO_3	7.15 ± 4.84	7.13 ± 4.94	7.06 ± 4.92	86.2	87.1	91.7	92.9
Aerosol NH_4^+	3.60 ± 1.77	4.06 ± 2.05	3.85 ± 1.99	94.8	96.0	98.5	98.8
Gas NH_3	0.74 ± 1.06	0.31 ± 0.79	0.50 ± 0.81	16.6	31.4	25.2	51.4
			At Pittsburgh Site (N = 313)^d				
Aerosol NO_3^-	2.09 ± 1.51	2.04 ± 1.74	1.98 ± 1.79	60.8	57.4	77.0	75.7
Gas HNO_3	1.01 ± 0.68	0.96 ± 0.78	1.02 ± 0.74	37.7	39.6	56.5	62.0
			At Clinton Site (N = 479)^e				
Aerosol NO_3^-	0.30 ± 0.26	0.28 ± 0.28	0.24 ± 0.27	58.0	47.2	71.8	62.0
Gas HNO_3	0.27 ± 0.25	0.29 ± 0.28	0.33 ± 0.30	52.4	49.3	78.7	69.5
Aerosol NH_4^+	1.15 ± 1.27	1.44 ± 1.57	1.42 ± 1.54	74.5	76.2	92.5	92.5
Gas NH_3	5.13 ± 4.73	4.86 ± 4.62	4.88 ± 4.63	95.4	96.5	97.5	97.9

[a]$\langle C \rangle$ is mean ± standard deviation ($\mu g\ m^{-3}$).
[b]The percentages of the comparison points whose model results are within a factor of 1.5 and 2.0 of the observations. N is number of samples.
[c]SO_4^{2-} = 12.17 ± 6.71, TNH_4 = 4.38 ± 2.39, TNO_3 = 7.57 ± 5.27, RH = 68.9 ± 19.9, T = 25.0 ± 3.3.
[d]SO_4^{2-} = 2.46 ± 1.14, TNH_4 = 1.74 ± 0.77, TNO_3 = 3.08 ± 2.18, RH = 67.1 ± 17.6, T = 3.9 ± 5.9.
[e]SO_4^{2-} = 3.64 ± 4.05, TNH_4 = 6.29 ± 5.51, TNO_3 = 0.57 ± 0.51, RH = 79.9 ± 14.2, T = 19.1 ± 7.7.

concentration is constrained and the aerosol fraction is dominant at the Pittsburgh site, both AIM and ISORROPIA can correctly predict the NO_3^- concentrations to within a factor of 2 of the observations for a majority of the data points (>76%), especially when NO_3^- concentrations are higher than 1.0 $\mu g\ m^{-3}$ (>89%) (see Figure 2). However, both models perform much more poorly on HNO_3, the gas fraction, as compared to the Atlanta situation. Figure 3 also shows that both models can reproduce diurnal variations of observed NO_3^- very well in most cases, except during a few days in which both models underpredict NO_3^- over the noon sampling periods (1000 to 1800 EST) (such as on days 1/2, 1/3, 1/10) and overpredict NO_3^- in the early morning (0000–0600 EST)

(such as on days 1/12, 1/16, 1/22). These AIM and ISORROPIA results are generally in agreement with *Takahama et al.* [2004], who used a thermodynamic model, GFEMN, to simulate the partitioning of $PM_{2.5}$ TNO_3 using the same data set at the Pittsburgh site.

[12] As shown in Figure 4 and Table 1, the results at the Clinton site are very different from those at both the Atlanta and Pittsburgh sites. The mean TNH_4 concentration (6.29 $\mu g\ m^{-3}$) at the Clinton site is about 1.5 times and 4 times higher than those at the Atlanta and Pittsburgh sites, respectively, whereas its mean SO_4^{2-} and TNO_3 concentrations are about 3 and 10 times lower than those at the Atlanta site, respectively (see Table 1). Most of the cases at
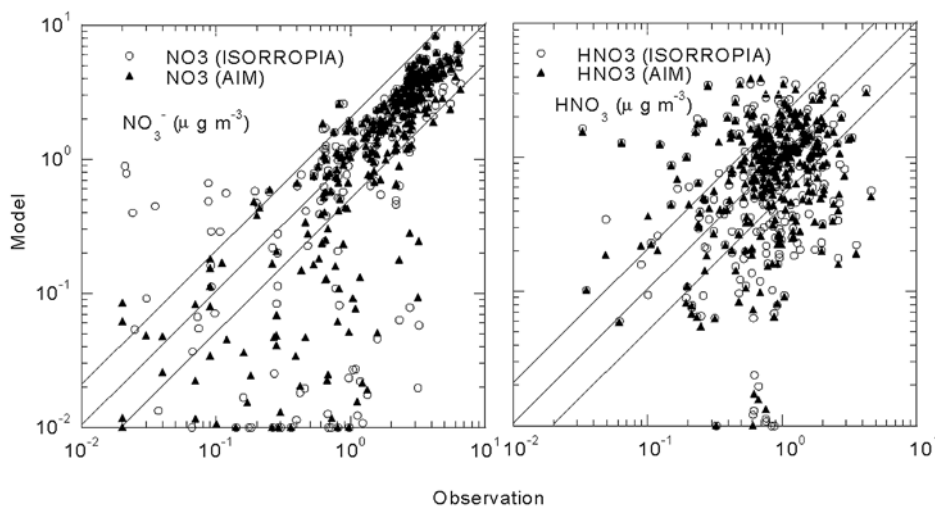

Figure 2. Same as Figure 1 but for aerosol NO_3^- and HNO_3 at the Pittsburgh site, PA, during the period of 2–31 January 2002.
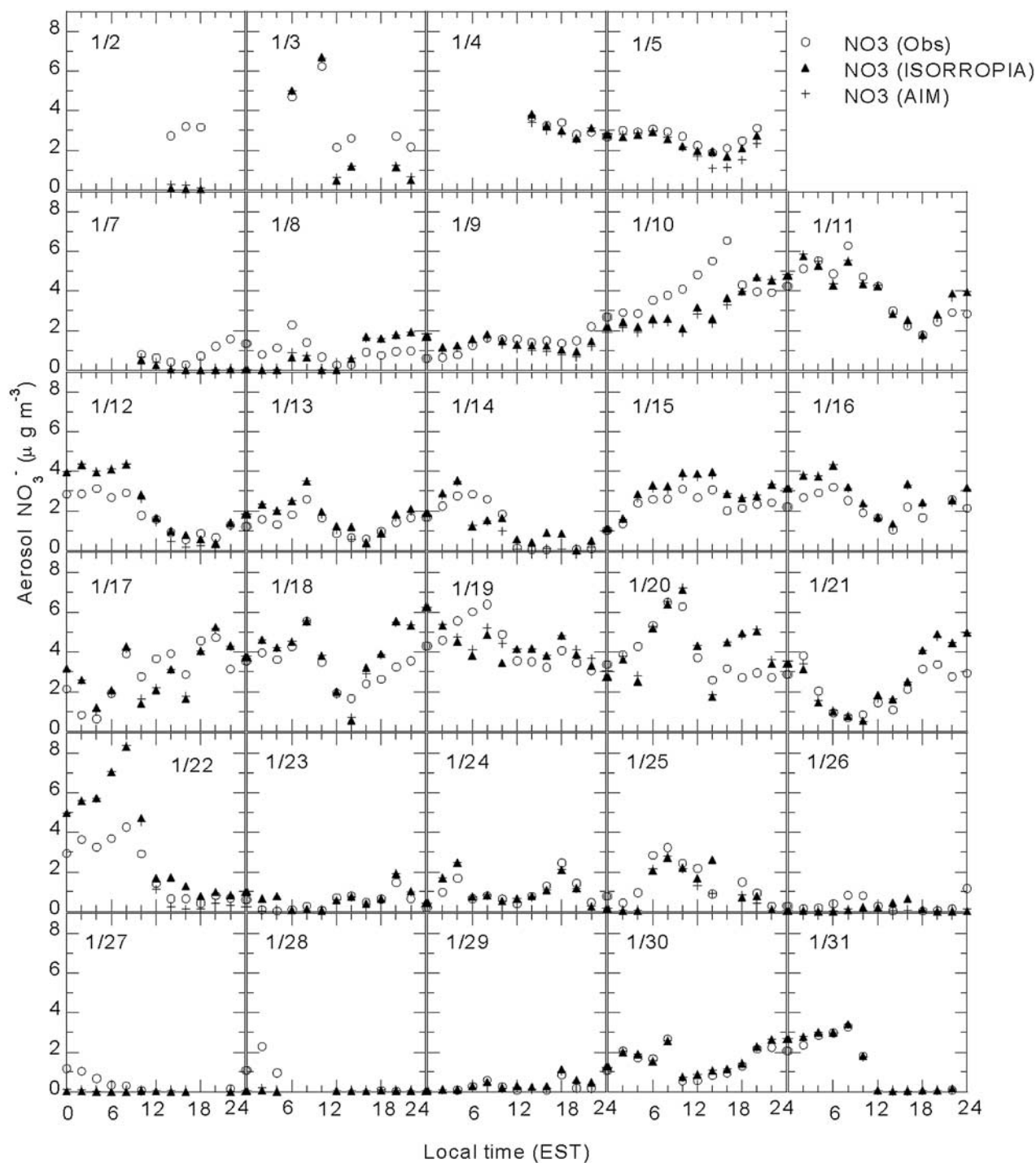
Figure 3. Time series of modeled and observed aerosol nitrate at the Pittsburgh site, PA, during the period of 2–31 January 2002.

the Clinton site are under very sulfate-poor conditions (the mean molar ratio of TNH_4 to SO_4^{2-} is 9.22), i.e., the system is alkaline. RH at the Clinton site is 20% higher than those at both the Atlanta and Pittsburgh sites. As shown in Figure 4, both models reproduced observed NH_3 concentrations very well (>95% within a factor of 1.5) and reproduced a majority of NH_4^+ concentration data points within a factor of 2 (>92%). Performance of both models for aerosol NO_3^-

at the Clinton site was better than at the Atlanta site but worse than at the Pittsburgh site.

3.1.2. Discussion of Possible Reasons for the Discrepancies Between the Model Predictions and Observations

[13] There are many possible reasons for the discrepancies between the model predictions and observations in partitioning of TNO_3 for aerosol NO_3^- in Figures 1, 2,
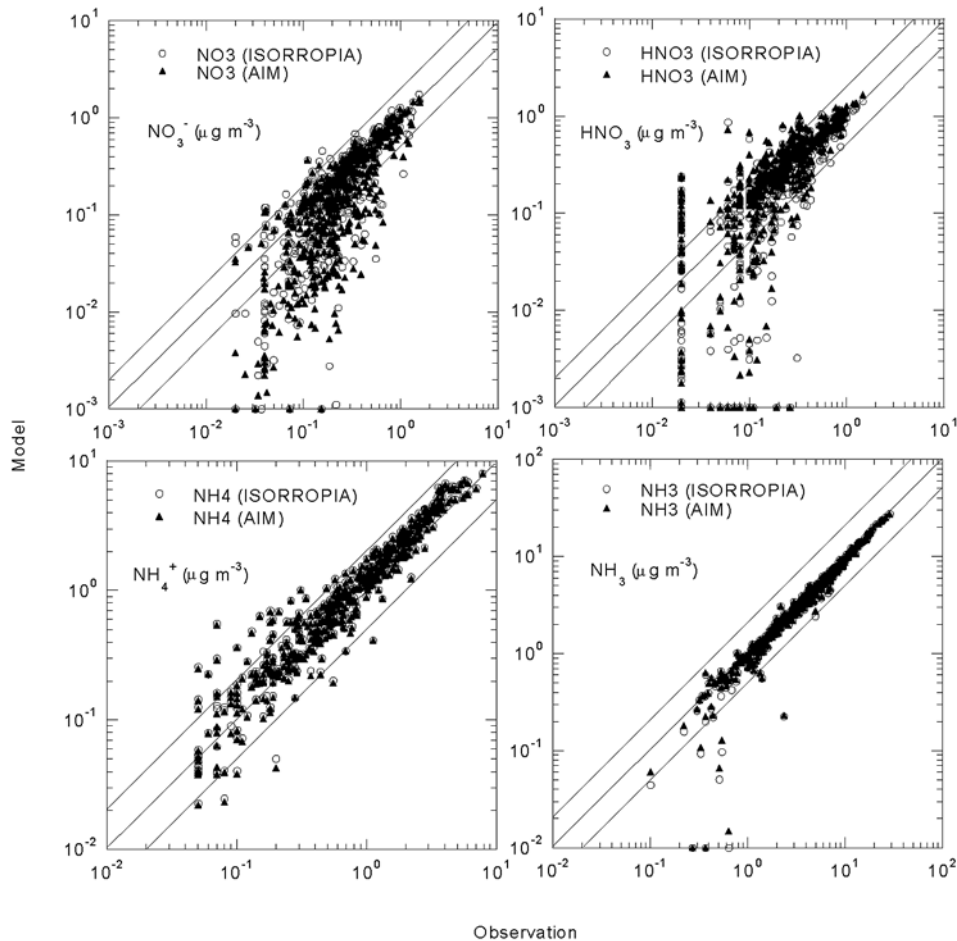
Figure 4. Same as Figure 1 but at the Clinton site, NC.

and 4. First, the measurement errors in SO_4^{2-} and TNH_4 can affect the model predictions. To show how each of these measurement errors can contribute to uncertainties in model predictions of aerosol NO_3^-, Gaussian (normally distributed) random errors are added to the input SO_4^{2-} and TNH_4 (base case concentrations, C_b) to create the sensitivity case concentrations (C_s) as follows

$$C_s = C_b + \varepsilon_p', \qquad (1)$$

where ε_p' represents truncated Gaussian random errors with zero mean and standard deviation equal to $15\% \times C_b$. An error of $\pm 15\%$ is used to correspond with the measurement uncertainty for both SO_4^{2-} and TNH_4 that was estimated as part of the U.S. EPA supersite program [*Solomon et al.*, 2003]. The errors are truncated so that only values within 2 standard deviations ($2 \times 15\% \times C_b$) are allowed. This gives a range within which we would expect the errors to be in all but about 5% of the most extreme cases. Gaussian random errors are chosen because measurement errors are generally considered to be independent and normally distributed [*Ripley and Thompson*, 1987]. Figure 5 shows the comparison of model predictions of the base case aerosol NO_3^- with those of the sensitivity case aerosol NO_3^- by ISORROPIA at the Atlanta site. The prediction results of

the ISORROPIA model for the test data sets before the introduction of errors are considered as the base case results. Note that the figure includes only 163 data points for which both ISORROPIA and AIM predict the existence of aerosol NO_3^- in Figure 1. It was found that the model with the measurement errors in both SO_4^{2-} and TNH_4 can only reproduce 61.3% of the base case aerosol NO_3^- within a factor of 2. Essentially the same pattern of error as shown in Figure 5 was obtained in more sensitivity tests with equation (1). These tests also showed that variation in measurement error that may be associated with different measurement averaging times does not significantly change these results, the relative change being less than 20%. This means that $\pm 15\%$ errors in SO_4^{2-} and TNH_4 translate into the model predictions of aerosol NO_3^- differing by more than a factor of 2 in many cases. This indicates that random errors in SO_4^{2-} and TNH_4 measurements can account for most of the discrepancies between the model predictions and observations of aerosol NO_3^- in Figure 1 at the Atlanta site. Similar conclusions can be obtained for the results at the Pittsburgh and Clinton sites and for the AIM model. This is generally in agreement with *Takahama et al.* [2004], who found that the measurement uncertainties in sulfate, total ammonia, nitrates and RH could account for most of the discrepancies between the model predictions and observations at the Pittsburgh site.
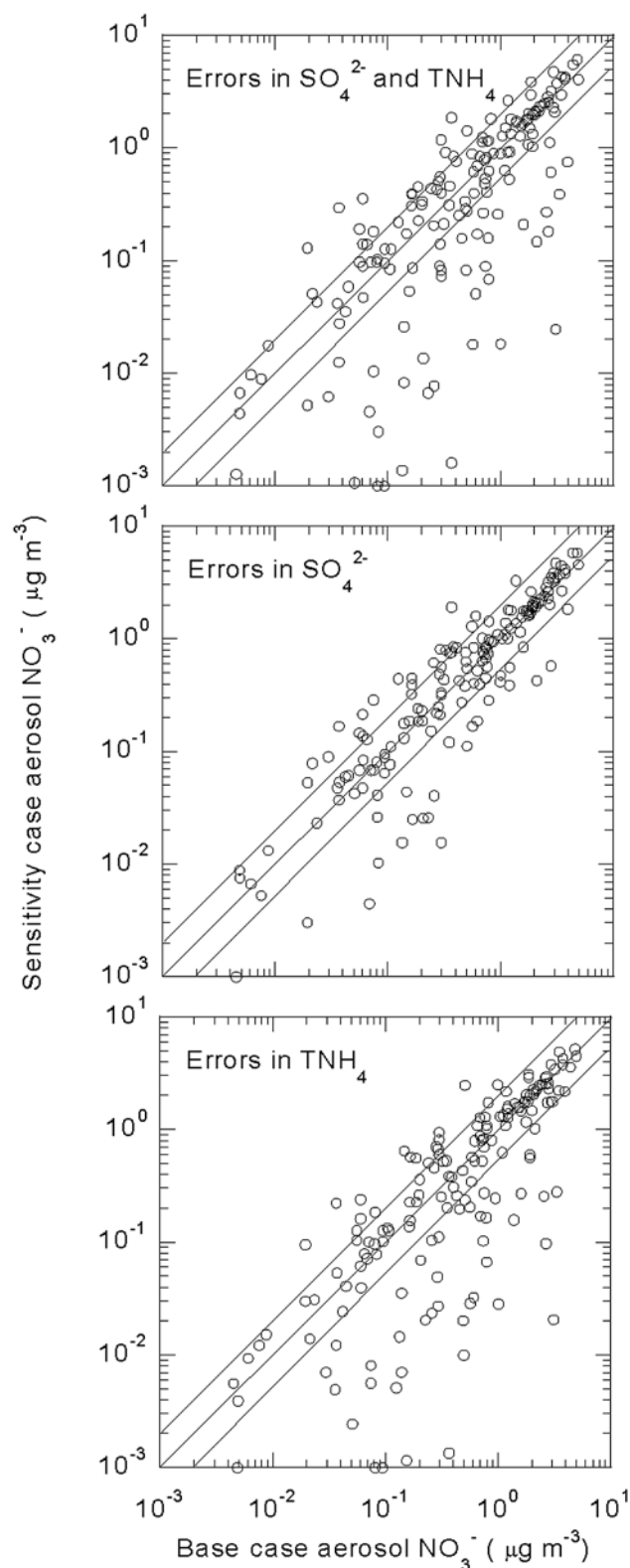
Figure 5. Sensitivity case NO_3^- with assumed Gaussian random errors in observed SO_4^{2-}, TNH_4 versus the base case NO_3^- for the ISORROPIA model at the Atlanta site.

[14] A second possible reason for the discrepancies is that a dynamic instead of an equilibrium model may be more suitable for some of these cases. For example, *Moya et al.* [2001] indicated that a dynamic instead of an equilibrium model could improve significantly the agreement between predictions and observations for NO_3^- for the cases with high temperatures and low RH values based on observations made during the 1997 IMADA-AVER study in Mexico City. Generally, as shown in Figure 6 for the Atlanta site, periods of NO_3^- overprediction are associated with conditions of lowest temperatures, high RH and sulfate-poor ($TNH_4/SO_4^{2-} > 2.0$) conditions, while those of underprediction are associated with the conditions of high temperature, low RH and sulfate-rich (molar ratio $TNH_4/SO_4^{2-} < 2.0$) conditions. This is in general agreement with *Moya et al.* [2001]. In another vein relating to coarse particles, *Meng and Seinfeld* [1996] found that the equilibrium time between particles and the gas phase increased with increasing particle size, extending up to several hours. *Meng and Seinfeld* [1996] indicated that after the gas phase approached equilibrium with the small particles, a substantial amount of the volatile compounds still transferred from the small particles to the large particles via the gas phase (dynamical transfer between small and large particles) and that atmospheric coarse aerosol particles might generally exist in nonequilibrium transition states. Aging of air masses, therefore, can favor the accumulation of NO_3^- in the coarse mode. At a coastal site in Hong Kong, China, *Zhuang et al.* [1999] found that 74% of total aerosol NO_3^- (fine plus coarse) was in the coarse mode.

[15] A third possible reason contributing to the discrepancies is that thermodynamic models are not able to accurately simulate the conditions encountered. *Ansari and Pandis* [2000] found that on average, thermodynamic models with the metastable state assumption (efflorescence behavior) predicted 11% higher NO_3^- concentrations than those with stable state assumption (deliquescence behavior) at low aerosol nitrate concentrations (<8 μg m^{-3}). ISORROPIA assumes that inorganic ions are internally mixed within $PM_{2.5}$; this may or may not lead to inaccuracies. *Takahama et al.* [2004] found that assuming that particles were external mixtures of crystallized and wetted particles during low RH period in July improved significantly agreement between the model predictions and observations at the Pittsburgh site.

[16] A fourth possible reason is that mechanisms other than thermodynamic equilibrium produce aerosol NO_3^-. A close inspection of Figures 1, 2, and 4 indicates that there are many cases in which the observations show the existence of low aerosol NO_3^- (such as 0.1 to 0.8 μg m^{-3}) but the thermodynamic models predicted negligible amounts of aerosol NO_3^- at the three sites. On the basis of single particle mass spectra taken during the 1999 Atlanta Supersite Experiment, *Lee et al.* [2003] found that the small local maximum of NO_3^- during the afternoon was associated mostly with particles containing soot/hydrocarbons or aluminosilicate components rather than the typical organic/sulfate particles. They believed that aerosol NO_3^- might be formed by the HNO_3 uptake or the heterogeneous reaction of NO_2 on soot and mineral particles.

[17] The approach used to test the equilibrium models is very important to the search for discrepancies. *Zhang et al.*
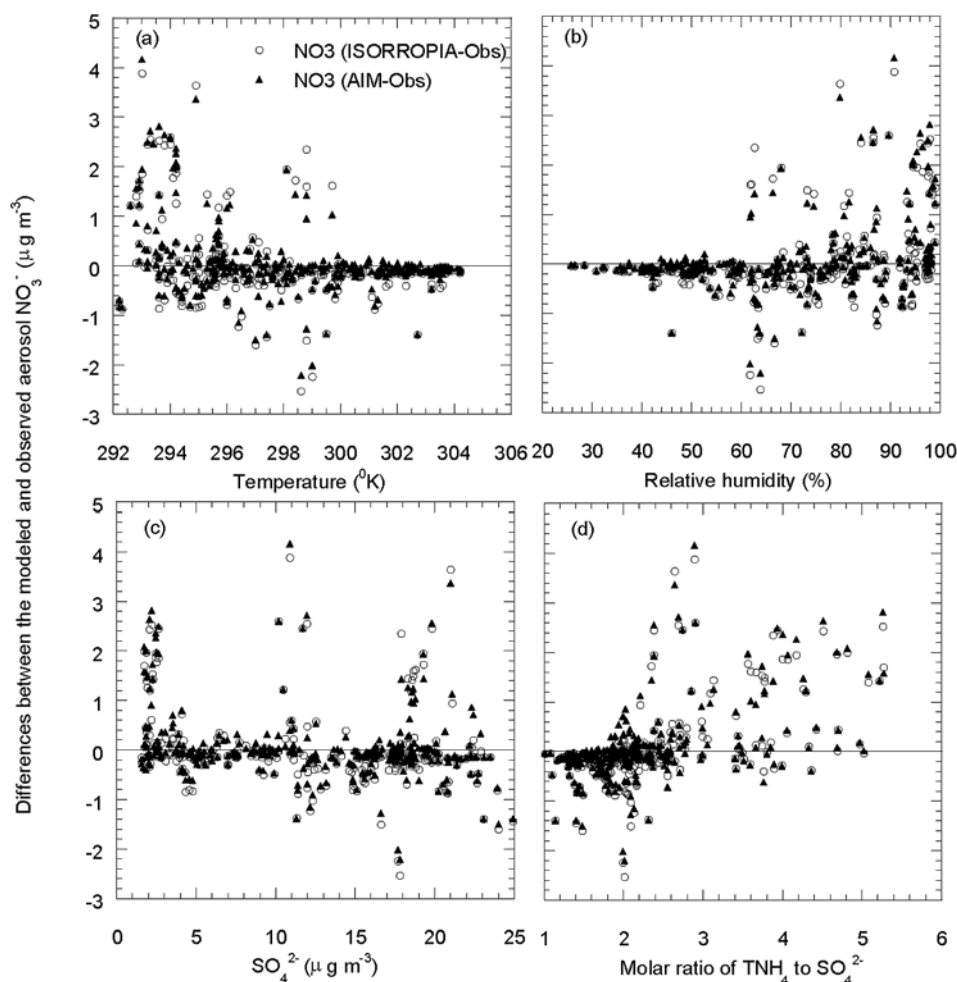
Figure 6. The differences between modeled and observed aerosol NO_3^- as a function of temperature, RH, SO_4^{2-} concentration, and molar ratio of TNH_4 to SO_4^{2-} at the Atlanta site.

[2003] used the same data sets at the Atlanta site to evaluate the thermodynamic equilibrium assumption for fine aerosol nitrate and ammonium with the ISORROPIA model in a reverse manner, i.e., they used observed aerosol NO_3^-, NH_4^+, SO_4^{2-}, Cl^- and Na^+ as inputs to calculate the equilibrium concentrations of gas HNO_3 and NH_3 and then compared the calculated gas HNO_3 and NH_3 concentrations with the observations. They found that the calculated equilibrium concentrations of HNO_3 and NH_3 were systematically higher and lower than the corresponding observations by more than a factor of 2, respectively [see *Zhang et al.*, 2003, Figures 4 and 5]. However, this is not consistent with the current results as shown in Figure 1, in which TNO_3, TNH_4 and SO_4^{2-} were used as inputs to ISORROPIA (in a forward manner) to calculate the equilibrium concentrations of HNO_3 and NH_3. As shown in Figure 1 and Table 1, ISORROPIA in the forward manner can reproduce 91.7% of observed HNO_3 within a factor of 2 (86.2% within a factor of 1.5), but underpredicts mean NH_3 by about a factor of 2. Figures 7a and 7b show that results for HNO_3 and NH_3 very close to those of *Zhang et al.* [2003] were obtained if ISORROPIA was run in the reverse manner with the data set used in this study. In this study, Na^+ and Cl^- data were not used due to the fact that the concentrations of Na^+ and Cl^- were very small relative to those of TNO_3, TNH_4 and SO_4^{2-}

at the Atlanta site and their omission does not affect the results. To investigate why the performance of ISORROPIA for HNO_3 and NH_3 predictions are so different in the forward and reverse manners for the same data set, sensitivity tests with assumed single fixed relative errors in aerosol NO_3^- and NH_4^+ were carried out for ISORROPIA in the reverse manner on the basis of observation data at the Atlanta site. As shown in Figures 7c, 7d, 7e, and 7f, −20% fixed errors in observed aerosol NH_4^+ or +30% fixed errors in observed aerosol NO_3^- can result in the ISORROPIA model in the reverse manner not being able to come within a factor of 2 for a majority of the HNO_3 and NH_3 data points as seen in the work of *Zhang et al.* [2003]. Unfortunately, *Zhang et al.* [2003] did not consider any possible effect of measurement errors in the aerosol NO_3^- and NH_4^+ on the predictions of HNO_3 and NH_3. As shown in Figure 1 and Table 1, most of the observed TNO_3 concentration at the Atlanta site is in the gas phase (93%). Since the aerosol NO_3^- concentrations are very low, the relative errors in the determination of aerosol NO_3^- should be much larger than those in the determination of TNO_3. This means that the errors in the measurement of aerosol NO_3^- and aerosol NH_4^+ may result in very large errors in the prediction of HNO_3 and NH_3 in the reverse manner as shown in Figure 7. Also, there are many cases in which ISORROPIA in the reverse
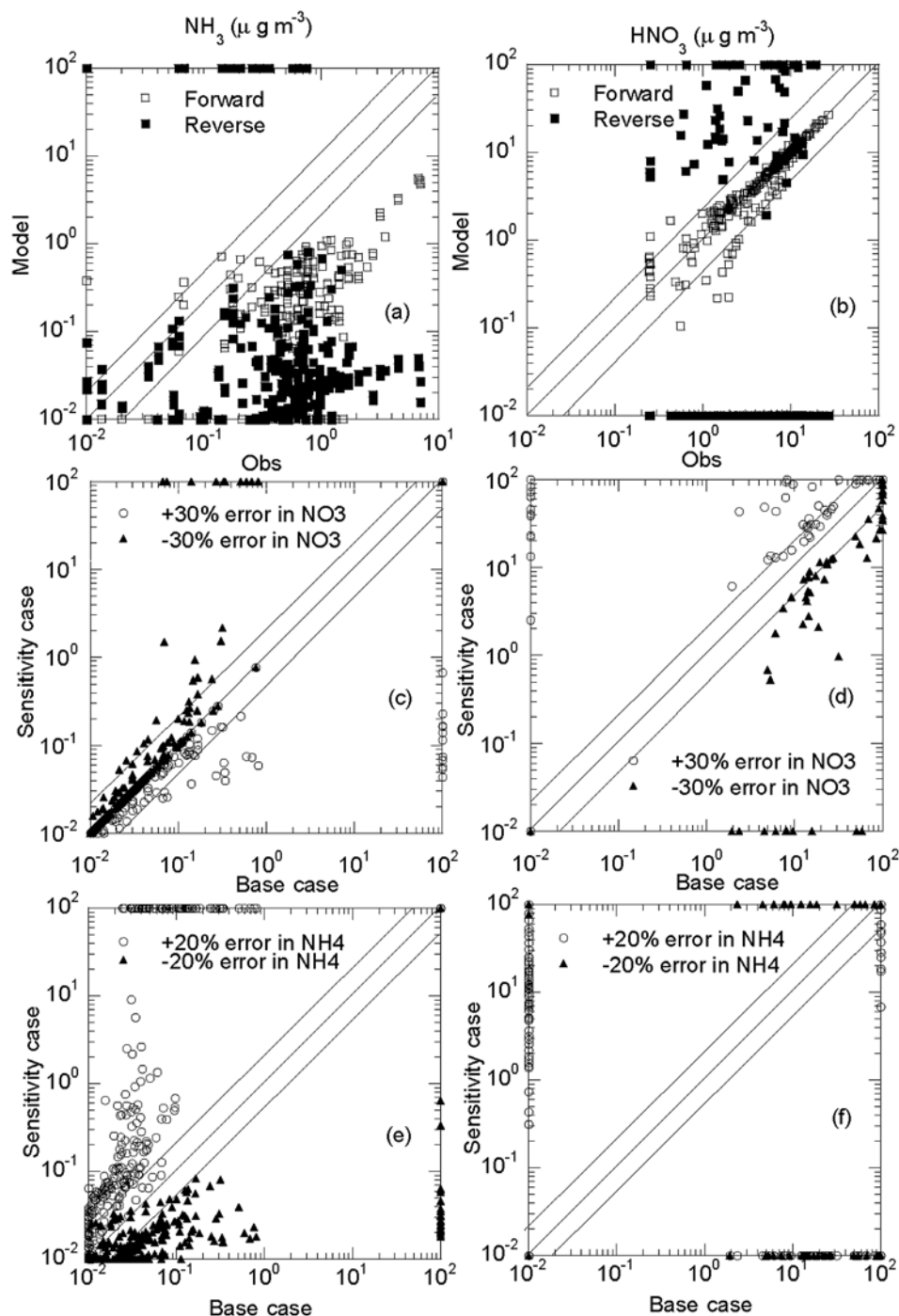
Figure 7. Comparison between the predictions of ISORROPIA in the forward and reverse manners and the observations for (a) NH_3 and (b) HNO_3 at the Atlanta site. (c–f) Comparisons of NH_3 and HNO_3 between the base case and sensitivity case with the fixed relative errors in aerosol NO_3^- ($\pm 30\%$) (Figures 7c and 7d) and in aerosol NH_4^+ ($\pm 20\%$) (Figures 7e and 7f) for ISORROPIA in the reverse manner (see text explanation).

manner predicted excessively high concentrations (e.g., 10000 μg m^{-3}) of HNO_3 and NH_3 as shown in Figure 7. Therefore it is preferable to use TNO_3, TNH_4 and SO_4^{2-} as inputs (in the forward manner) to evaluate the thermodynamic equilibrium assumption rather than using only aerosol concentrations (in the reverse manner).

3.2. Performance of the 3-D Air Quality Model (CMAQ) for SO_4^{2-} and TNH_4

[18] One of the major objectives for this study is to assess the ability of 3-D air quality models, with current thermodynamic equilibrium modules, to predict aerosol NO_3^-.
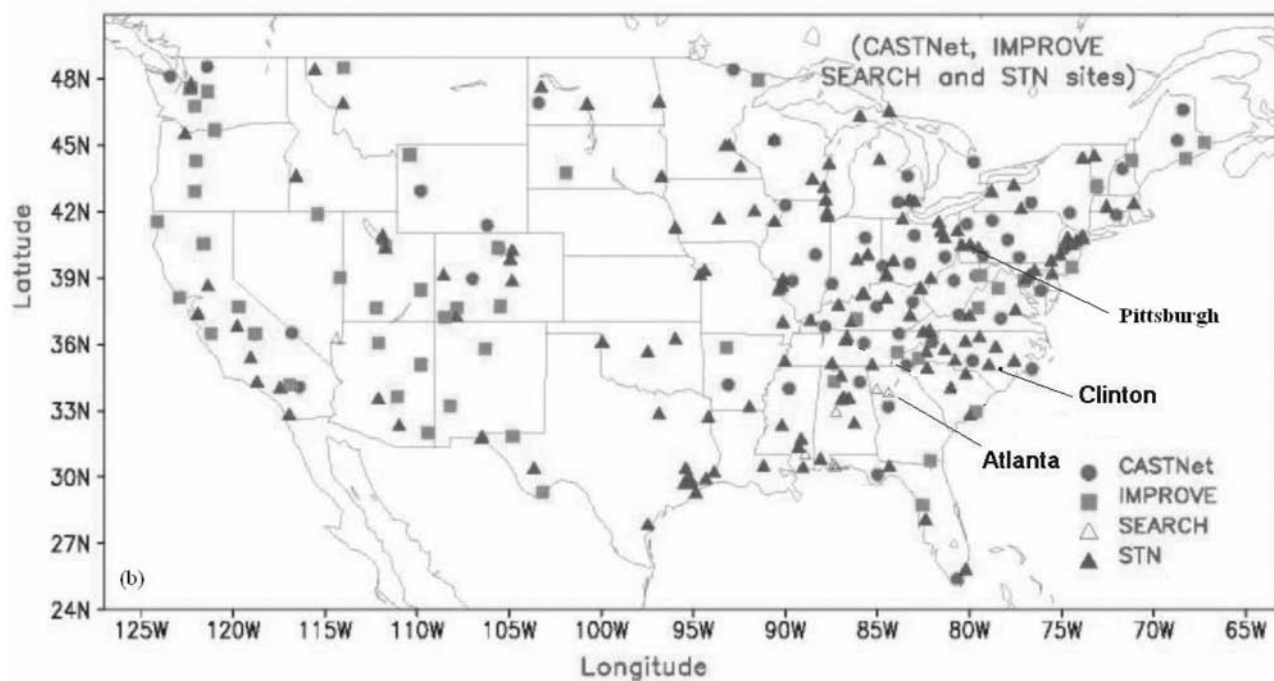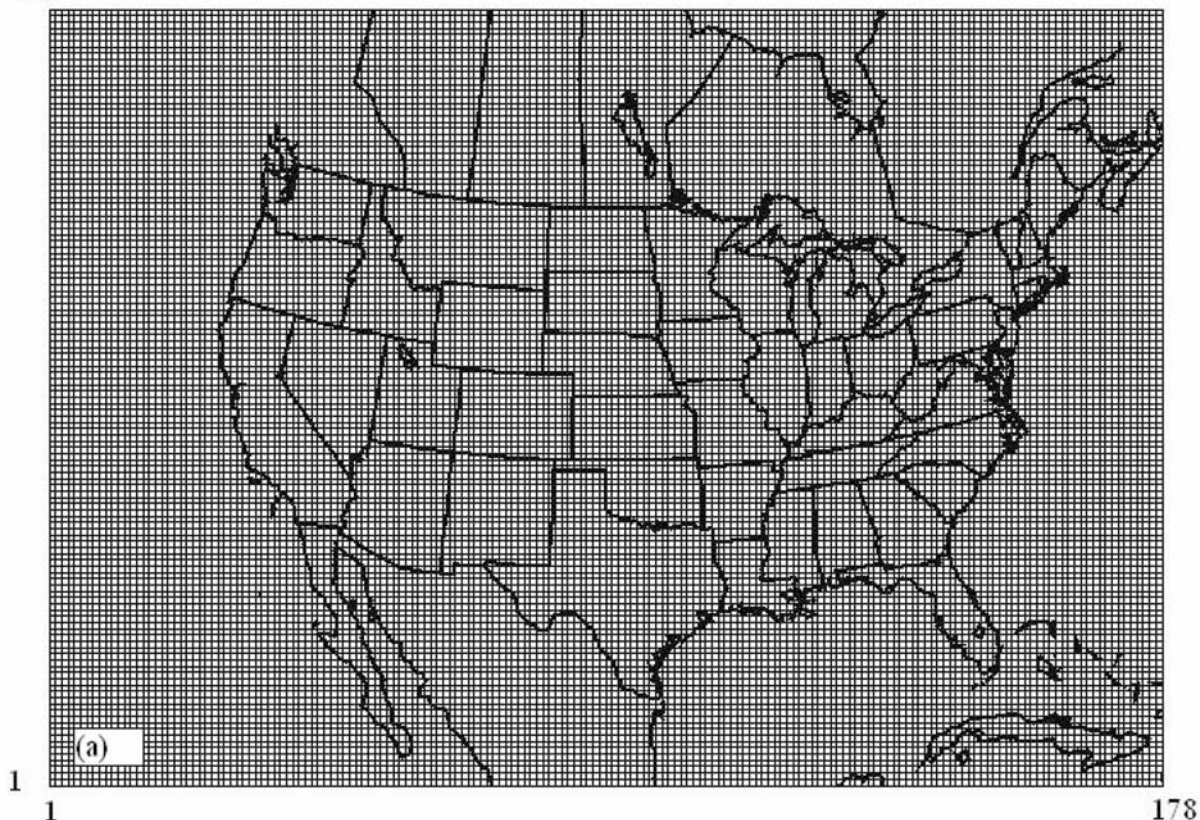
Figure 8. (a) The model domain and (b) locations of CASTNet, IMPROVE, SEARCH, and STN network sites, Atlanta, Pittsburgh, and Clinton sites over the United States. See color version of this figure at back of this issue.
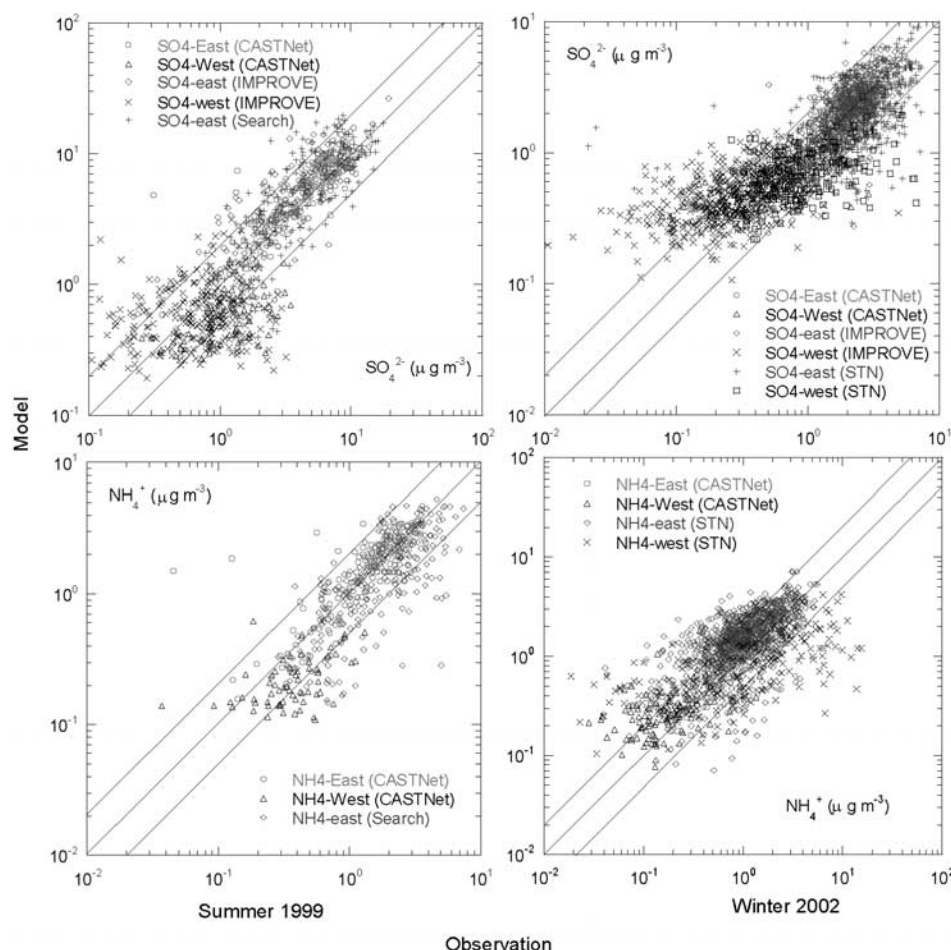
Figure 9. Comparisons of the results of CMAQ model with the observations for aerosol SO_4^{2-} and NH_4^+ for different networks over the United States during 15 June to 17 July 1999 (summer 1999) and 5 January to 18 February 2002 (winter 2002). See color version of this figure at back of this issue.

3.2.1. Regional Performance Over the United States

[19] Error in 3-D model predictions is typically much larger than error in the measurements. To assess 3-D model performance, the 3-D model errors in SO_4^{2-} and TNH_4 predictions need to be quantified and their effects on aerosol NO_3^- predictions characterized as these two species are the most significant parameters in partitioning TNO_3 between the aerosol and gas phases. For reference relevant to the present study, the model performance of the U.S. EPA Models-3/CMAQ model system [*Byun and Ching*, 1999] on $PM_{2.5}$ SO_4^{2-}, NH_4^+ and NO_3^-, gas HNO_3 and TNO_3 is summarized for the summer (15 June to 17 July) of 1999 and winter (5 January to 18 February) of 2002 over the United States. A detailed description of the model run is given by *Yu et al.* [2004]. The model domain covers the continental United States with a horizontal grid of 178 × 124 32 km grid cells (see Figure 8a). The vertical resolution is 21 layers, which are set on a sigma coordinate, from the surface to ∼100 mb. The model is driven by meteorological fields from the fifth Generation Pennsylvania State/National Center for Atmospheric Research Mesoscale Meteorological Model (MM5) [*Grell et al.*, 1994]. The approach to aerosol microphysical modeling simulates the particle distribution function (PDF) by a multimodal approach, in which particle size distributions are represented as the superposition of three lognormal subdistributions, or modes [*Binkowski and Roselle*, 2003]. The aerosol processes performed in the CMAQ model include primary emissions, nucleation-condensation, coagulation, dry and wet depositions, and cloud processing (including aqueous chemistry). Emissions of gas-phase SO_2, CO, NO, NO_2, NH_3, VOC and primary $PM_{2.5}$ are from the 1999 EPA National Emissions Inventory (NEI99 version 1) (http://www.epa.gov/ttn/chief/). The SAPRC-99 gas-phase chemical mechanism where the lumped VOC classes are derived from VOCs present in the NEI99 is used [*Carter*, 2000]. As shown in Figure 8a, boundaries of the model domain are located over the ocean or remote areas. The concentrations of all species were set to be those of clear tropospheric air conditions for initial and boundary conditions. A model spin-up period of 3 days was used to mitigate the effects of initial conditions on the model results. The modeled concentrations at the grids at which the observation sites are located are used to compare to the observations.

[20] The observational data used in this evaluation include: (1) data at 61 rural sites from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. Two 24-hour samples are collected on quartz
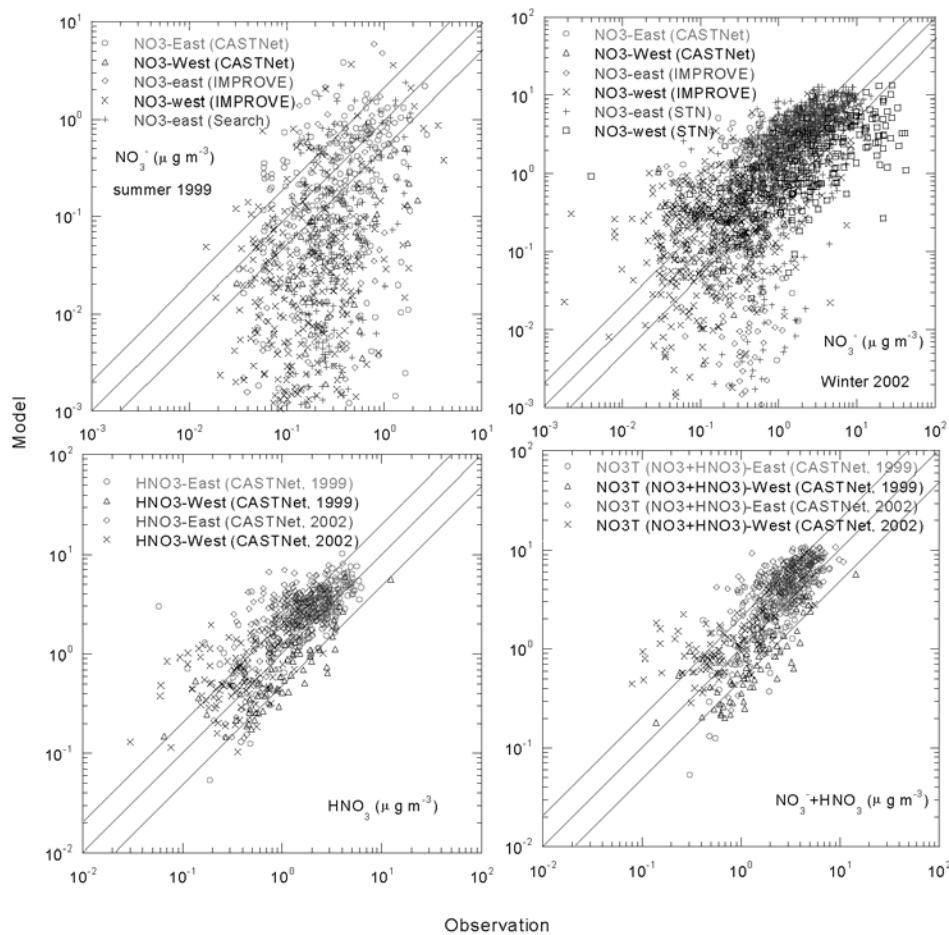
Figure 10. Same as Figure 9 but for aerosol NO_3^-, gas HNO_3, and total nitrate (i.e., aerosol NO_3^- + HNO_3). See color version of this figure at back of this issue.

Table 2. Statistical Summaries of the Comparison of the Model Results of EPA Models-3/CMAQ With the Observations of Different Networks for Aerosol SO_4^{2-}, NH_4^+, and NO_3^-, Gas HNO_3, and Total Nitrate (TNO_3) Over the United States From 15 June to 17 July 1999 (summer), and From 5 January to 18 February 2002 (Winter)[a]

Parameters	$\langle C \rangle$,[b] 1999 Observation	Model	$\langle C \rangle$,[b] 2002 Observation	Model	Percent Within a Factor of 1.5[c] 1999	2002	Percent Within a Factor of 2[c] 1999	2002
			CASTNet: N = 265 for 1999, N = 413 for 2002					
Aerosol SO_4^{2-}	4.57	4.92 (0.888)	1.71	1.76 (0.841)	69.3	78.8	83.7	94.2
Aerosol NH_4^+	1.37	1.45 (0.865)	0.84	1.18 (0.850)	72.0	51.1	86.0	81.2
Aerosol NO_3^-	0.50	0.32 (0.284)	1.38	2.19 (0.758)	23.9	30.1	35.6	50.8
Gas HNO_3	2.26	2.43 (0.778)	1.26	2.28 (0.684)	63.6	28.9	81.8	57.8
TNO_3	2.72	2.71 (0.756)	2.61	4.43 (0.798)	59.5	34.2	78.0	66.3
			IMPROVE: N = 424 for 1999, N = 683 for 2002					
Aerosol SO_4^{2-}	2.07	2.43 (0.890)	0.98	1.17 (0.860)	45.8	46.6	67.7	71.2
Aerosol NO_3^-	0.27	0.16 (0.310)	0.69	0.91 (0.540)	10.6	18.9	17.2	32.5
			STN: N = 1044 for 2002					
Aerosol SO_4^{2-}			2.23	1.88 (0.670)		59.6		83.2
Aerosol NH_4^+			1.45	1.58 (0.390)		39.5		61.1
Aerosol NO_3^-			3.35	3.38 (0.360)		30.7		48.9

[a]The correlation equations between model predictions and observations on the log scale over the eastern United States (longitude > 100°N; see Figure 7) for all networks are also listed (r is correlation coefficient and RMSE is root mean square error). For summer 1999 (N = 343 over the eastern United States): SO_4^{2-}, ln[Model] = 0.855ln[Obs] + 0.379, r = 0.863, RMSE = 0.7448; NH_4^+, ln[Model] = 0.922ln[Obs] + 0.109, r = 0.880, RMSE = 0.3224. For winter 2002 (N = 1334 over the eastern United States): SO_4^{2-}, ln[Model] = 0.741ln[Obs] + 0.125, r = 0.691, RMSE = 0.4364; NH_4^+, ln[Model] = 0.633ln[Obs] + 0.353, r = 0.669, RMSE = 0.6552.
[b]$\langle C \rangle$ is the mean concentration ($\mu g\ m^{-3}$), and the values in parentheses are correlation coefficients between the model predictions and observations.
[c]Percentages of the comparison points whose model results are within a factor of 1.5 and 2 of the observations. N is number of samples.
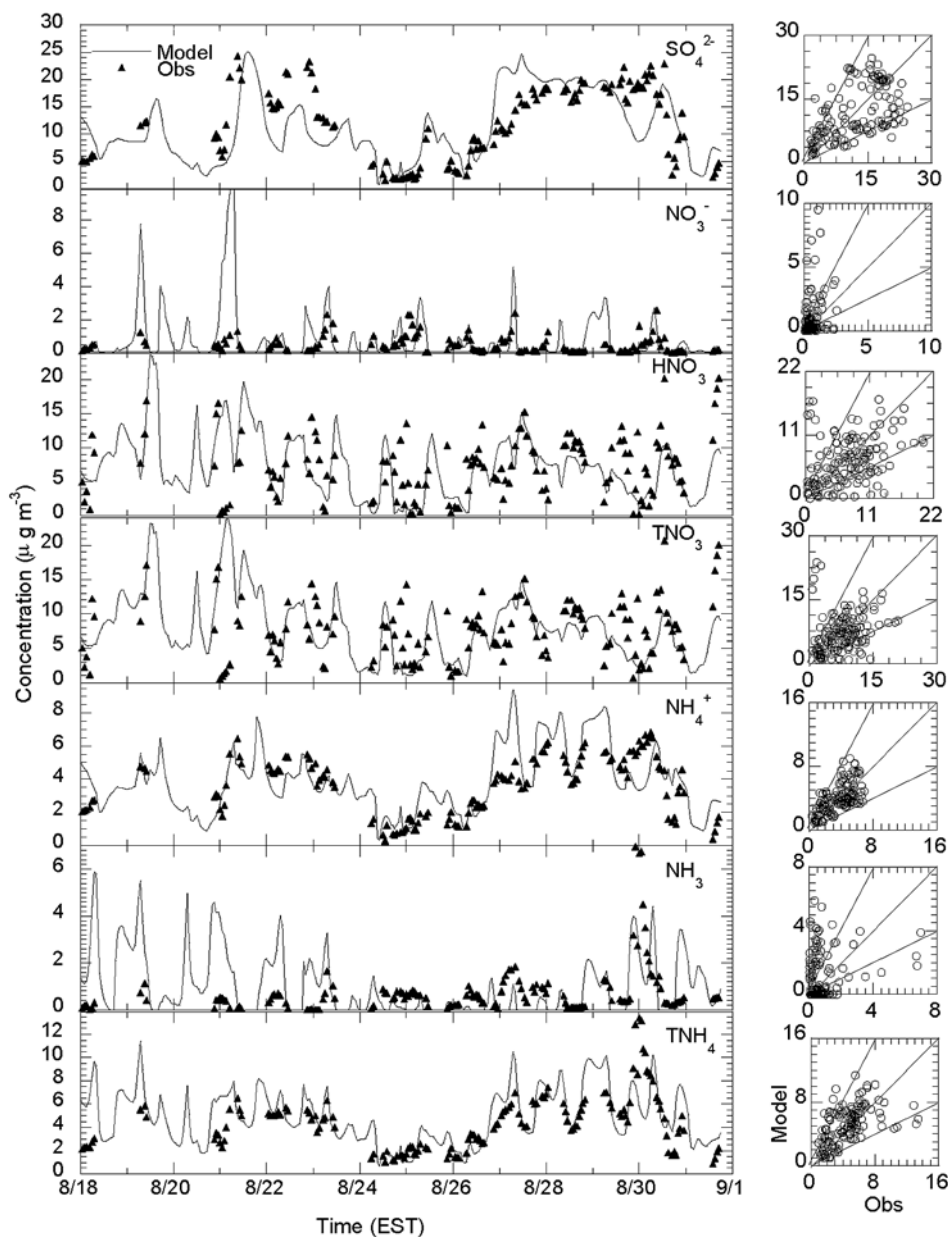
Figure 11. Time series of 3-D CMAQ model predictions and observations for SO_4^{2-}, NO_3^-, HNO_3, TNO_3, NH_4^+, NH_3, and TNH_4 at the Atlanta site (1999).

filters each week, on Wednesday and Saturday, beginning at midnight local time [*Malm et al.*, 1994]. (2) data at 73 rural sites from the Clean Air Status and Trends Network (CASNet). Weekly (Tuesday to Tuesday) samples are collected on Teflon filters. (3) data at 153 urban sites from the Speciated Trends Network (STN). Twenty-four-hour samples are usually taken once every six days, but some states choose to collect data every third day, beginning between 0800 and 1000 local time (LT). Figure 8b shows the locations of the stations whose observations were used in this study.

[21] Table 2 summarizes the results, and the scatterplots of model results vs. observations paired in time and space are shown in Figures 9 and 10. Generally, the CMAQ reproduced CASTNet observations better than other net-

works, because the sampling duration of the CASTNet network is a week, as opposed to 24 hours for the IMPROVE and STN networks, even though there is a concern about nitrate volatilization during sampling. On the basis of results in Figure 9 and Table 2, it can be seen that CMAQ predictions are close to being within a factor of 2 of the weekly SO_4^{2-} observations for CASTNet summer and winter and STN winter (84%, 94% and 83%, respectively). A majority, 60–80%, are within a factor of 1.5. Seventy percent of the SO_4^{2-} predictions are within a factor of 2 for the 24-hour rural observations of IMPROVE. The agreement for aerosol NH_4^+ tends to follow that of SO_4^{2-} because most of the NH_4^+ is associated with SO_4^{2-}. Thus, while the CMAQ can capture well the large-scale features, the model has difficulty in very accurately predicting (better
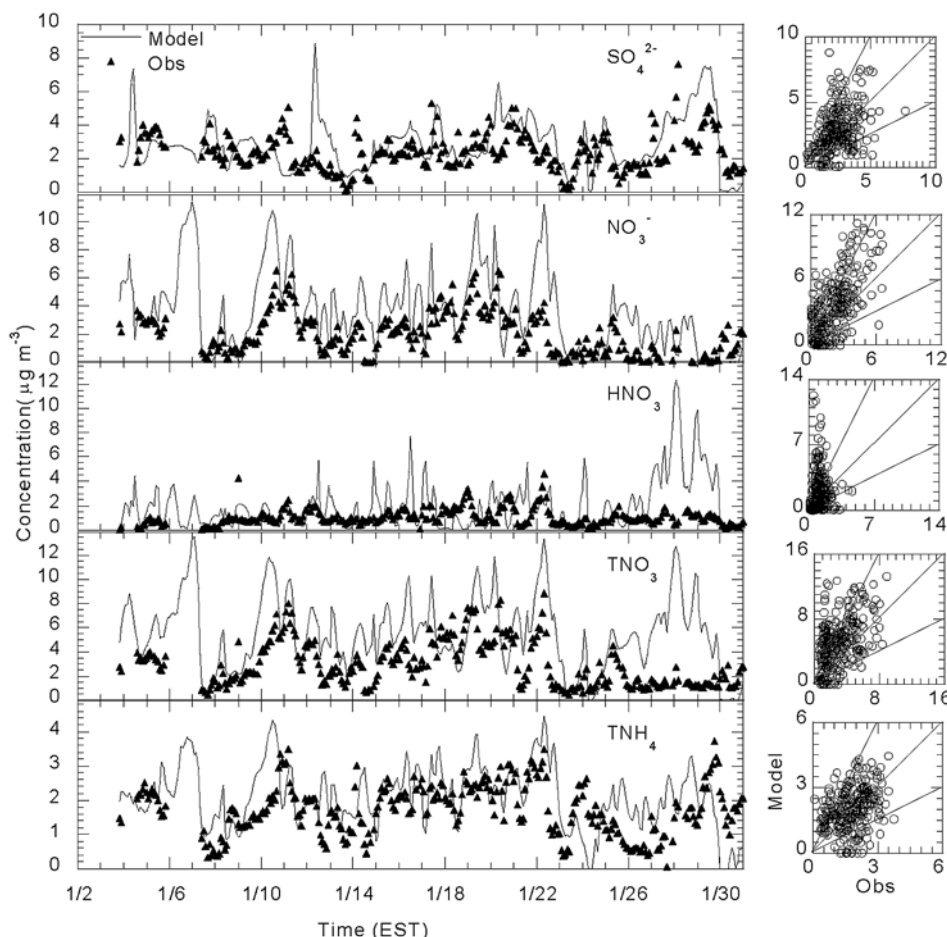
Figure 12. Same as Figure 11 but at the Pittsburgh site (2002).

than a factor of 1.5) the day-by-day and spatial variations in sulfate. The agreement between CMAQ and observations is poorest for aerosol NO_3^- (see Figure 10 and Table 2). At best 50% of the model predictions are within a factor of 2 of observations and at worst only 20% are within a factor of 2 (see Table 2). As analyzed quantitatively below, one of the major reasons for the poorer performance on aerosol NO_3^- is the error in the predictions of SO_4^{2-} and TNH_4. Such errors can cause overprediction or underprediction of aerosol NO_3^- by more than a factor of 2 even though the model may simulate TNO_3 correctly. Figure 10 and Table 2 also show that the CMAQ performances for HNO_3 and TNO_3 are better for 1999 summer than 2002 winter on the basis of the CASTNet observations.

3.2.2. Time Series Performance at Each of the Three Special Sites

[22] On a more detailed temporal scale, Figures 11, 12, and 13 show time series comparisons and scatterplots of the CMAQ predictions and observations for SO_4^{2-}, NO_3^-, HNO_3, TNO_3, NH_4^+, NH_3 and TNH_4 at the Atlanta, Pittsburgh and Clinton sites, respectively. At the Atlanta and Pittsburgh sites, which have sufficient temporal resolution to resolve the diurnal variations, the CMAQ model is capturing with a good deal of fidelity the hourly variations and broad synoptic changes seen in the observations of SO_4^{2-}, although with occasional major excursions. None-

theless, the scatter of the paired comparisons for SO_4^{2-} is larger than a factor of 2 about the one-to-one line (75% of the comparisons are within a factor of 2) (see Table 3). The same holds true for TNH_4 where also 75% of the comparisons are within a factor of 2 but major excursions exist. However, the predictions of CMAQ for aerosol NO_3^- are noticeably worse. The CMAQ mean NO_3^- concentration is roughly a factor of 1.6 too high for both sites. The percent of comparisons within a factor of 2 is only 30% and 49% for Atlanta and Pittsburgh, respectively. The pattern of NO_3^- overprediction at Pittsburgh follows the pattern of TNH_4 overprediction, but with what appears to be an amplification. At the Clinton site, the CMAQ model captured general temporal variations of SO_4^{2-} most of the time (50% within a factor of 2) and the model mean (7.69 μg m^{-3}) is also close to the observed mean (6.30 μg m^{-3}). However, the CMAQ overpredicted observed TNO_3 and TNH_4 systematically most of the time, resulting in the systematic overpredictions of NO_3^-, HNO_3, NH_4^+, and NH_3. The analysis at the more highly resolved temporal scale indicates that the models are capable of capturing the broad patterns, especially those of SO_4^{2-} and TNH_4, and quite capable of simulating the longer-term average concentrations. Yet, while we have confidence in the model's equilibrium formulation, accurate predictions of hourly NO_3^- are difficult to obtain due to emissions uncertainty, among other
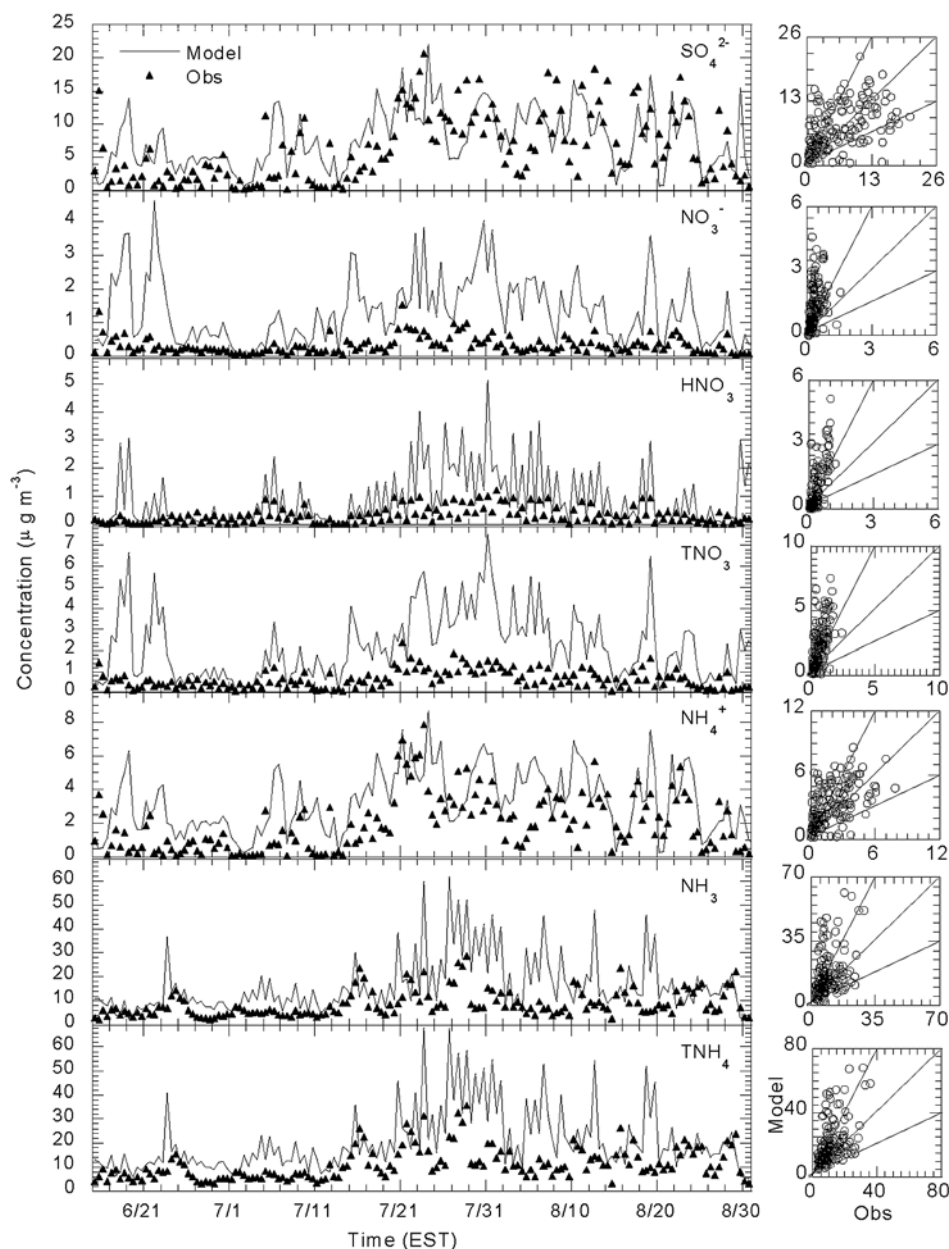
Figure 13. Same as Figure 11 but at the Clinton site (1999).

uncertainties, and the meteorological model's imprecision at replicating the meteorology.

3.3. Effects of 3-D Model Prediction Errors in SO_4^{2-}, TNH_4, Temperature, and Relative Humidity on Predicting Aerosol NO_3^-

[23] As shown in section 3.2, the 3-D CMAQ model can only reproduce 46–79% of SO_4^{2-} and 39–72% of aerosol NH_4^+ within a factor of 1.5 (see Tables 2 and 3). This means that the 3-D air quality models are frequently making errors on the order of ±50% in the simulations of SO_4^{2-} and NH_4^+. In order to test how much these and other errors will affect the predictions of aerosol NO_3^-, a test data set containing 163 data points, in which both ISORROPIA and AIM predict the existence of aerosol NO_3^-, was obtained from the 325 observations at the Atlanta site.

We refer to this case as the summer case. The winter case consists of 312 data points from the 313 observations at the Pittsburgh site. The predicted aerosol NO_3^- concentrations of each thermodynamic model for the test data sets before the introduction of errors in the inputs are considered as the base case concentrations.

3.3.1. Gaussian Random Errors in SO_4^{2-} and TNH_4

[24] As shown in Figure 9 and Table 2, there is substantial linear correlation between the 3-D model predictions and observations on a log scale for both SO_4^{2-} and NH_4, i.e., correlation coefficient >0.67. As can be seen in Figure 9, the spread of errors is roughly homogeneous on the log scale, especially over the eastern United States. In addition, the errors in the prediction of SO_4^{2-} are basically uncorrelated with the TNH_4 prediction errors (not shown). To test how much the errors in SO_4^{2-} and TNH_4 associated with the

Table 3. Same as Table 2 but at the Atlanta (18–31 August 1999), Pittsburgh (5–31 January 2002) and Clinton (15 June to 31 August 1999) Sites

Parameters	$\langle C \rangle$[a]		Percent Within a Factor of 1.5[b]	Percent Within a Factor of 2[b]
	Observation	Model		
Atlanta: N = 147 for 1999				
Aerosol SO_4^{2-}	12.01	11.57 (0.566)	46.3	74.1
Aerosol NH_4^+	3.59	3.93 (0.640)	61.2	88.4
Gas NH_3	0.76	1.05 (0.201)	9.5	12.2
TNH_4	4.39	5.04 (0.554)	61.9	79.6
Aerosol NO_3^-	0.54	0.82 (0.340)	17.0	29.9
Gas HNO_3	7.16	6.48 (0.377)	44.2	62.6
TNO_3	7.59	7.20 (0.241)	51.0	67.3
Pittsburgh: N = 305 for 2002				
Aerosol SO_4^{2-}	2.43	2.84 (0.413)	48.9	73.4
TNH_4	1.75	2.01 (0.333)	53.4	72.1
Aerosol NO_3^-	1.97	3.26 (0.673)	28.5	48.5
Gas HNO_3	1.03	1.89 (0.069)	24.9	39.0
TNO_3	2.96	5.12 (0.484)	30.2	52.8
Clinton: N = 155 for 1999				
Aerosol SO_4^{2-}	6.30	7.69 (0.474)	36.8	50.3
Aerosol NH_4^+	1.95	3.25 (0.529)	29.7	46.5
Gas NH_3	8.77	16.26 (0.411)	34.8	58.7
TNH_4	11.24	20.47 (0.510)	32.3	61.3
Aerosol NO_3^-	0.33	1.33 (0.400)	7.1	15.5
Gas HNO_3	0.32	0.91 (0.750)	20.6	33.5
TNO_3	0.65	2.22 (0.610)	9.0	17.4

[a]$\langle C \rangle$ is the mean concentration ($\mu g\ m^{-3}$), and the values in parentheses are correlation coefficients between the model predictions and observations.
[b]Percentages of the comparison points whose model results are within a factor of 1.5 and 2 of the observations. N is number of samples.

predictions from the 3-D air quality model such as CMAQ will affect the predictions of aerosol NO_3^- in the thermodynamic model, sensitivity case concentrations (C_s) of SO_4^{2-} and TNH_4 are generated by adding independent Gaussian (normally distributed) random errors to their base case (original) concentrations (C_b) as follows:

$$\ln(C_s) = \ln(C_b) + \varepsilon, \qquad \varepsilon \sim G(0, \sigma = RMSE), \qquad (2)$$

where ε represents Gaussian random errors with zero mean and standard deviation equal to the RMSE, the root mean square error. The RMSE used in this study is obtained from comparisons of the paired 3-D model predictions and observations as shown in Table 2 for each species (SO_4^{2-} and NH_4^+). Note that the values of RMSE in Table 2 are only for the results of the eastern United States because both the Atlanta and Pittsburgh sites are located in the eastern United States. The RMSE value for NH_4^+ in Table 2 is used for TNH_4 because NH_3 is not measured in each network. Figure 14 shows the sensitivity case input concentrations generated by equation (2) compared to the base case input concentrations of test data sets for SO_4^{2-} and TNH_4 in the summer and winter cases. As can be seen in Figure 14, the pattern of scatter of Figure 9 (only for results of the eastern United States, red and blue symbols) is qualitatively reproduced. The comparison of predictions of aerosol NO_3^- between the sensitivity case and the base case is shown in Figure 15 and summarized in Table 4. Essentially the same results like those in Figure 15 and Table 4 are obtained for companion sensitivity tests with equation (2) (not shown). The equilibrium models with the 3-D air quality model-derived random errors in SO_4^{2-} and TNH_4 can only predict

<50% and <62% of aerosol NO_3^- within a factor of 1.5 and 2, respectively, as shown in Table 4, although the modeled means are close to the observations. For ISORROPIA in Table 4, 47% and 60% of the NO_3^- predictions from the sensitivity cases are within a factor of 2 of the base case for Atlanta and Pittsburgh, respectively. These percentages are similar to, although somewhat higher than, the 30% and 49% of the NO_3^- predictions that are within a factor of 2 given in Table 3 for Atlanta and Pittsburgh, respectively. This study suggests that a large source of error in predicting aerosol NO_3^- stems from the errors in 3-D model predictions of SO_4^{2-} and TNH_4 for the eastern United States. There is an important similarity between Figures 15 and 10 for the aerosol NO_3^-. For summer 1999 there are evidently additional sources of error as discussed in section 3.1.2, most likely not random, contributing to the severe underpredictions of NO_3^- for many of the points in Figure 10. Also, NH_3 emissions were highly uncertain, both temporally and spatially [*Gilliland et al.*, 2003]. Very large, systematic underprediction biases between CMAQ monthly averaged predictions of rainwater concentrations of NH_4^+ and NADP measurements have been found. These biases can cover geographical domains the size of one to several states and add to the difficulty in predicting aerosol NO_3^-. Table 4 and Figure 15 also indicate that errors in TNH_4 are more critical than errors in SO_4^{2-} to prediction of NO_3^- and that the higher the NO_3^- concentration, the less sensitive the predicted NO_3^- concentrations are to the errors in SO_4^{2-} and TNH_4. These results indicate that the ability of 3-D models to simulate aerosol NO_3^- concentrations is limited by uncertainties in predicted SO_4^{2-} and TNH_4.

[25] An additional sensitivity study with the different combinations of single, fixed relative errors of ±50% in
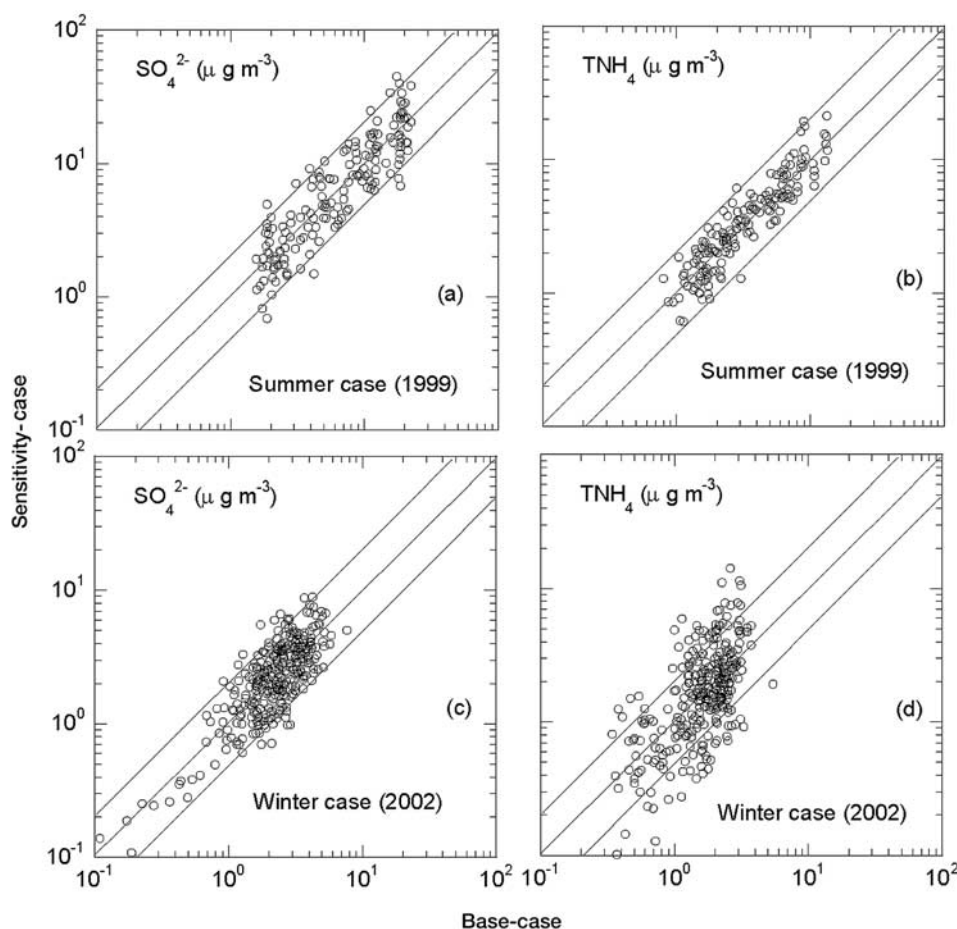
Figure 14. Comparison of base case SO_4^{2-} and TNH_4 with those of the sensitivity cases created by the Gaussian random errors on the basis of observational data sets at the Atlanta site (upper panels for the summer case (1999)) and Pittsburgh site (lower panels for the winter case (2002)) (see text for an explanation).

SO_4^{2-} and TNH_4 are also carried out with the test data sets (not shown here). The fixed relative errors of ±50% were chosen because the 3-D CMAQ model can only reproduce 46–79% of SO_4^{2-} and 39–72% of aerosol NH_4^+ within a factor of 1.5 as discussed previously. Both ISORROPIA and AIM gave similar responses in the predicted aerosol NO_3^- to the single relative fixed errors in SO_4^{2-} and TNH_4. It was found that the error in aerosol NO_3^- was amplified relative to the input error. For example, both ISORROPIA and AIM underpredicted almost all aerosol NO_3^- concentrations by more than a factor of 2 for −50% errors in TNH_4, and could not reproduce a majority of aerosol NO_3^- data points within a factor of 2 (<40%) for +50% error in SO_4^{2-}. This sensitivity investigation also indicated that the predicted aerosol NO_3^- concentrations in the winter case are less sensitive to errors in SO_4^{2-} and TNH_4 than in the summer case because the aerosol NO_3^- concentrations are much higher, and SO_4^{2-} and TNH_4 concentrations are much lower in the winter case when compared to those in the summer case (see Table 1). The results also indicate that errors in TNH_4 are more critical than errors in SO_4^{2-} to prediction of NO_3^- as shown in Figure 15.

3.3.2. Errors in Temperature and Relative Humidity

[26] Table 5 shows the comparison of sensitivity case NO_3^- for single fixed relative errors of ±10% individually in temperature and RH with those of the base case in the summer and winter times. In contrast to large effects from the errors in SO_4^{2-} and TNH_4, the responses of the aerosol NO_3^- predictions are less sensitive to errors in temperature and RH. Generally, both models can reproduce a majority of the aerosol NO_3^- data points within a factor of 1.5 if there are only ±10% errors in temperature and RH, especially for the winter times, with somewhat more sensitivity to errors in RH. However, ±20% errors in both temperature and RH can result in neither model being able to reproduce a majority of aerosol NO_3^- data points within a factor of 1.5 (percentage <42%) (not shown) although both models can still capture 53–69% of aerosol NO_3^- within a factor of 2 in the summer case. For the winter case, the predicted aerosol NO_3^- is much less sensitive to errors in temperature and RH. This may be due to the fact that temperatures in the winter times are very low (3.9 ± 5.9 °C), and most of TNO_3 concentration is in the aerosol phase. This is generally in agreement with *Takahama et al.* [2004], who found that errors in temperature measurements do not contribute significantly to model errors when temperatures are low and most of the nitrate concentration is in the aerosol phase. They also found that measurement errors in RH can contribute significantly to model errors
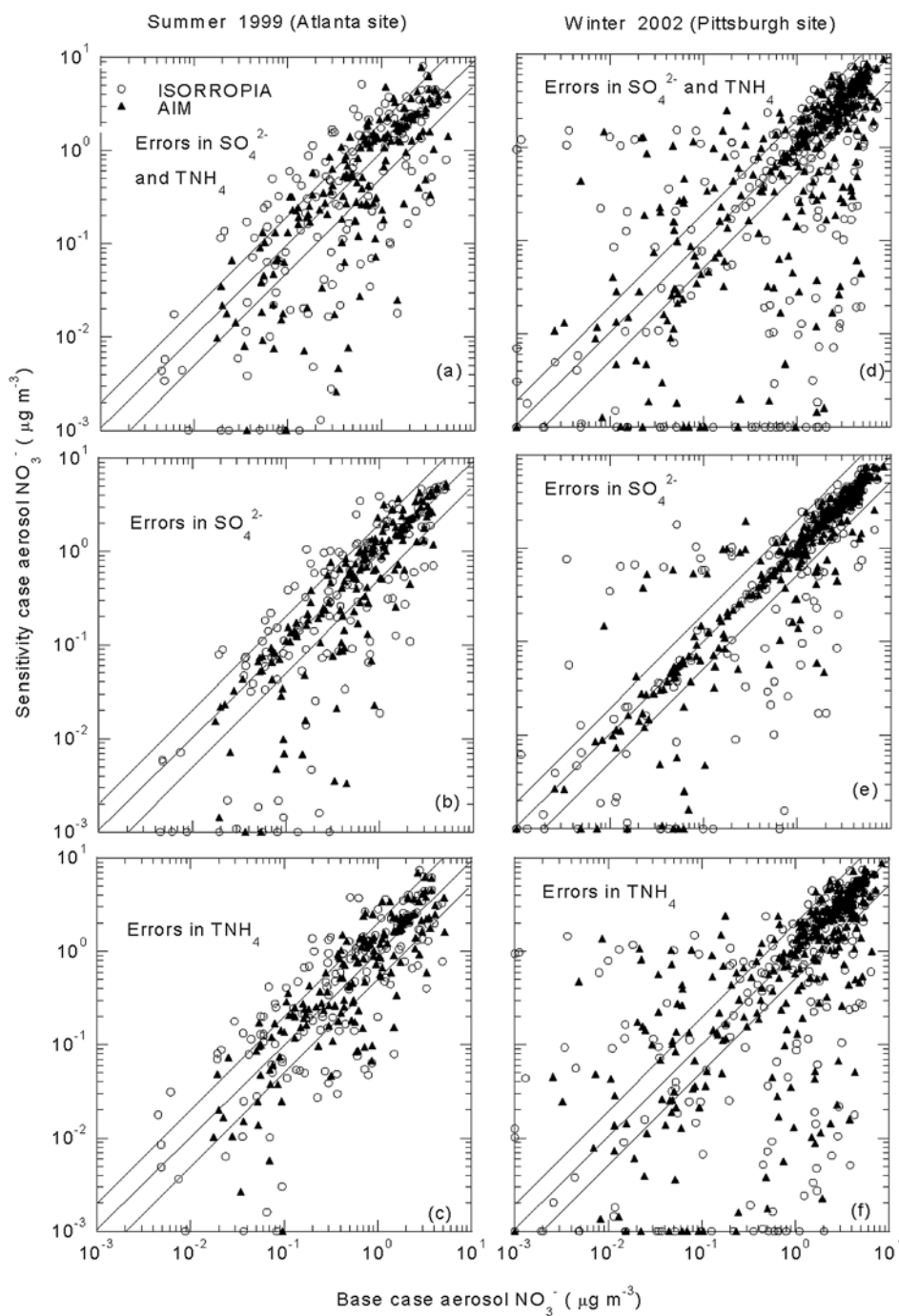
Figure 15. Sensitivity case NO_3^- with assumed Gaussian random errors in SO_4^{2-}, TNH_4 versus the base case NO_3^- for AIM and ISORROPIA for (a−c) the summer case and (d−f) the winter case.

for NO_3^- prediction when particles are assumed to be liquid or RH is close to a transition point between solid and liquid aerosols.

4. Conclusions

[27] Two thermodynamic equilibrium models, ISORRO-PIA and AIM, have been evaluated by comparing the modeled partitioning of TNO_3 and TNH_4 between gas and aerosol phases with that of observations using high time-resolution measurement data obtained during the 1999 Atlanta Supersite Experiment (summer case) and the 2002 Pittsburgh Air Quality Study (PAQS) Supersite Experiment (winter case), and 12-hour measurement data at the Clinton site, NC, in 1999. Generally, ISORROPIA and AIM performed similarly in the partitioning of TNO_3 and TNH_4 for these three data sets in most cases, with some differences because of differences in the calculation of chemistry and multicomponent activity coefficients in the two models. The capability of thermodynamic models to reproduce the

Table 4. Statistical Summaries of the Comparisons of the Modeled (ISORROPIA and AIM) Aerosol NO_3^- for the Different Sensitivity Cases Created by the Gaussian Random Errors (See Text Explanation) Versus Those of the Base Cases on the Basis of Observational Data at the Atlanta Supersite (Summer Case) and Pittsburgh Supersite (Winter Case)

Condition	$\langle C \rangle$[a]			Percent Within a Factor of 1.5[b]		Percent Within a Factor of 2[b]	
	Base Case	ISORROPIA	AIM	ISORROPIA	AIM	ISORROPIA	AIM
Summer Case With Atlanta Data: N = 163							
Gaussian errors in SO_4^{2-} and TNH_4	0.99 ± 1.12	1.11 ± 1.38	1.11 ± 1.34	30.1	40.5	47.2	62.6
Gaussian errors in SO_4^{2-}	0.99 ± 1.12	1.03 ± 1.26	1.05 ± 1.22	43.6	58.9	59.5	71.2
Gaussian errors in TNH_4	0.99 ± 1.12	1.10 ± 1.35	1.12 ± 1.30	34.4	42.3	54.6	68.1
Winter Case With Pittsburgh Data: N = 312							
Gaussian errors in SO_4^{2-} and TNH_4	2.00 ± 1.72	1.80 ± 1.84	1.80 ± 1.85	48.4	48.1	60.3	60.3
Gaussian errors in SO_4^{2-}	2.00 ± 1.72	1.93 ± 1.78	1.91 ± 1.82	70.2	75.6	77.6	84.3
Gaussian errors in TNH_4	2.00 ± 1.72	1.81 ± 1.84	1.82 ± 1.86	48.1	46.8	61.2	61.9

[a]$\langle C \rangle$ is the mean ± standard deviation of NO_3^- concentration ($\mu g\ m^{-3}$).
[b]Percentages of the comparison points whose sensitivity-case results are within a factor of 2 (or 1.5) of the base case results. N is the number of sensitivity cases.

observed partitioning of TNO_3 and TNH_4 between gas and aerosol phases differed from site to site depending on chemical and meteorological conditions at the site. For example, at the Atlanta site, for NH_4^+ 94% and 96% of ISORROPIA and AIM predictions are within a factor of 1.5 of observations, respectively. For HNO_3, 86 and 87% of ISORROPIA and AIM predictions are within a factor of 1.5 of observations. However, neither model reproduced a majority of observed aerosol NO_3^- and gas NH_3 within a factor of 2 (NO_3^-: <48% and NH_3: <51%) at the Atlanta site. At the Pittsburgh site, both models can predict a majority of NO_3^- data points within a factor of 2 (>76%), especially when NO_3^- concentrations are higher than 1.0 $\mu g\ m^{-3}$ (>89%), whereas both models perform more poorly on HNO_3 than at the Atlanta site. It was also found that both models reproduced the main features of the diurnal variations of observed NO_3^- in most cases reasonably well, except that both models underpredict NO_3^- over the noon sampling periods (1000–1800 EST) and overpredict NO_3^- in the early morning (0000–0600 EST) in some days at both the Atlanta and Pittsburgh sites. At the Clinton site,

both models reproduced observed NH_3 concentrations very well (>95% within a factor of 1.5), and performed a little better on aerosol NO_3^- (47–58% within a factor of 1.5) than at the Atlanta site but less than at the Pittsburgh site. The different chemical and meteorological conditions at the three sites can explain why both models perform differently in partitioning of TNO_3 and TNH_4. There are many different possible reasons for the discrepancies between the models and observations in partitioning of TNO_3. The sensitivity test indicates that in many cases measurement uncertainties in SO_4^{2-} and TNH_4 can explain a major fraction of the discrepancies between the model predictions and observations in partitioning of TNO_3.

[28] Comparison of the 3-D air quality model (CMAQ) predictions with the observations over the United States indicates that the performance of the CMAQ model for SO_4^{2-} is fairly reasonable spatially and temporally. However, its performance for NO_3^-, HNO_3, NH_4^+, and NH_3 strongly depends on its performance for TNO_3, TNH_4 and SO_4^2. Sensitivity tests show that random errors associated with SO_4^{2-} and TNH_4 predictions of the 3-D model can

Table 5. Statistical Summaries of the Comparison of the Modeled (ISORROPIA and AIM2) Aerosol NO_3^- for Sensitivity Cases With Different Single Fixed Relative Errors in Temperatures and Relative Humidity Versus Those of Base Cases on the Basis of Observational Data at the Atlanta Supersite, GA (Summer Case) and the Pittsburgh Site (Winter Case)

Cases	Condition	$\langle C \rangle$[a]			Percent Within a Factor of 1.5[b]		Percent Within a Factor of 2[b]	
		Base Case	ISORROPIA	AIM	ISORROPIA	AIM	ISORROPIA	AIM
	Summer Case With Atlanta Data: N = 163							
1	+10% error in temperature (°C)	0.99 ± 1.12	0.83 ± 1.01	0.87 ± 1.02	69.9	67.5	97.5	99.4
2	−10% error in temperature (°C)	0.99 ± 1.12	1.14 ± 1.20	1.24 ± 1.20	77.9	72.4	100.0	99.4
3	+10% error in RH (%)	0.99 ± 1.12	2.11 ± 2.86	2.17 ± 2.80	60.1	54.6	69.9	73.0
4	−10% error in RH (%)	0.99 ± 1.12	0.59 ± 0.76	0.58 ± 0.69	58.9	56.4	68.7	66.9
	Winter Case With Pittsburgh Data: N = 312							
1	+10% error in temperature (°C)	1.98 ± 1.79	2.03 ± 1.74	1.95 ± 1.79	98.1	98.4	99.7	99.0
2	−10% error in temperature (°C)	1.98 ± 1.79	2.07 ± 1.73	1.99 ± 1.78	98.1	98.1	99.4	99.0
3	+10% error in RH (%)	1.98 ± 1.79	2.12 ± 1.79	2.01 ± 1.81	89.7	94.9	95.8	97.4
4	−10% error in RH (%)	1.98 ± 1.79	2.01 ± 1.72	1.89 ± 1.77	88.1	92.3	95.2	96.1

[a]$\langle C \rangle$ is mean ± standard deviation of NO_3^- concentration ($\mu g\ m^{-3}$).
[b]Percentages of the comparison points whose sensitivity case results are within a factor of 2 (or 1.5) of the base case results. N is the number of sensitivity cases.

result in the thermodynamic model calculation replicating only 47% and 60% of the base case NO_3^- within a factor of 2 for summer and winter cases, respectively. This suggests that a large source of error in predicting aerosol NO_3^- stems from the errors in 3-D model predictions of SO_4^{2-} and TNH_4 for the eastern United States. This study shows that the higher the NO_3^- concentration, the less sensitive the predicted NO_3^- concentrations are to the errors in SO_4^{2-} and TNH_4 in both winter and summer cases. It was found that errors in TNH_4 are more critical than errors in SO_4^{2-} to prediction of NO_3^- and that the responses of the aerosol NO_3^- predictions are not very sensitive to the errors in temperature and RH under the tested conditions. The ability of 3-D models to simulate aerosol NO_3^- concentrations is limited by uncertainties in predicted SO_4^{2-} and TNH_4. While there is feedback between partitioning and the levels of predicted TNO_3, errors in TNO_3 are much less sensitive to these uncertainties and 3-D models are capable of predicting TNO_3 with accuracy comparable to that of SO_4^{2-} or TNH_4.

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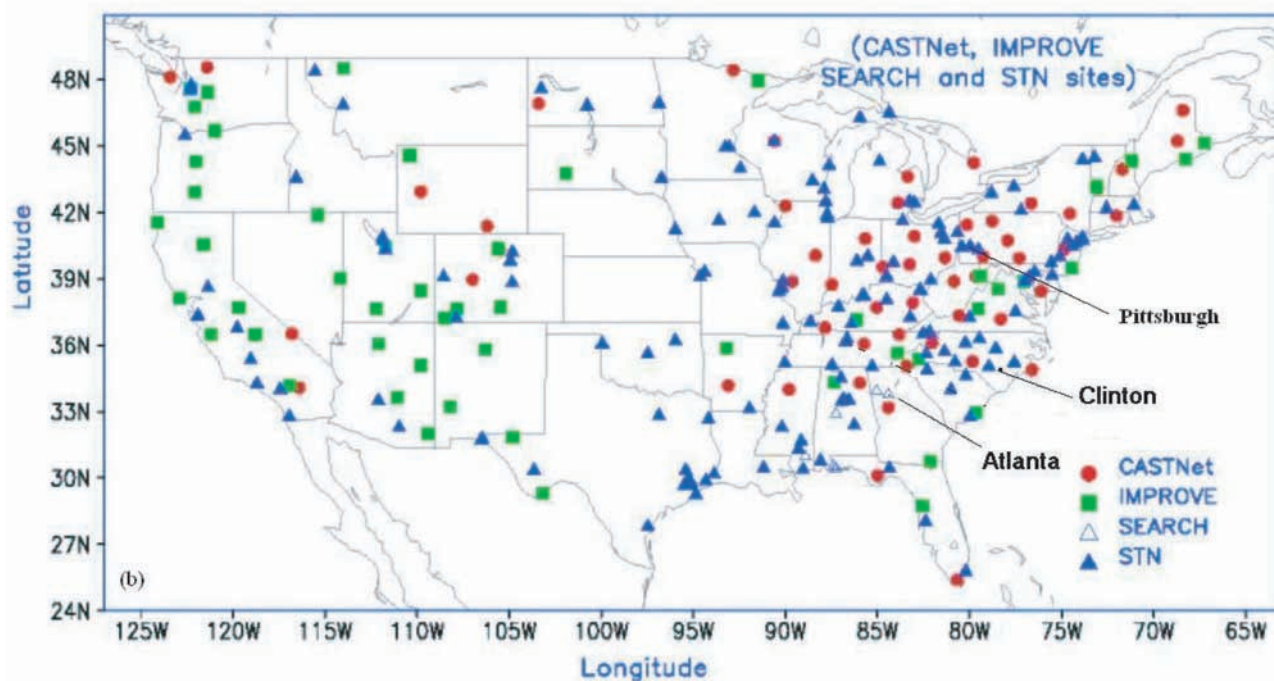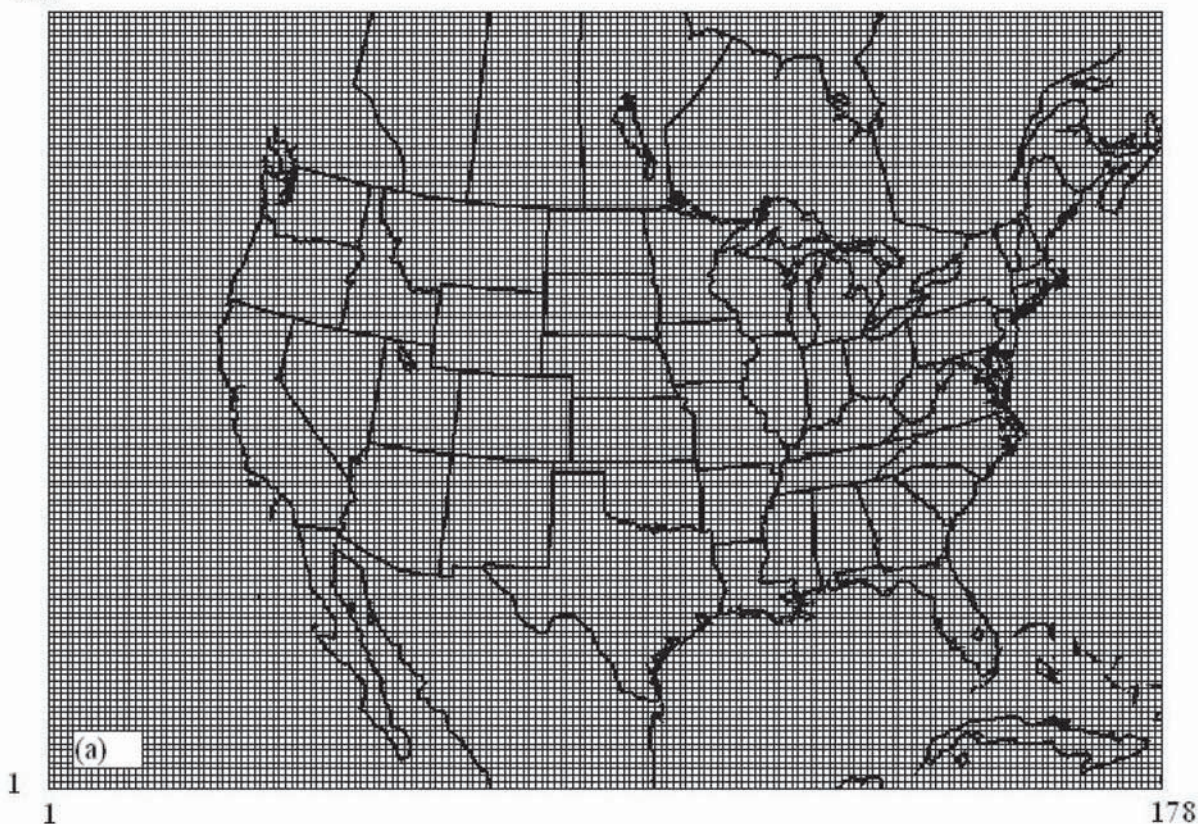
Figure 8. (a) The model domain and (b) locations of CASTNet, IMPROVE, SEARCH, and STN network sites, Atlanta, Pittsburgh, and Clinton sites over the United States.
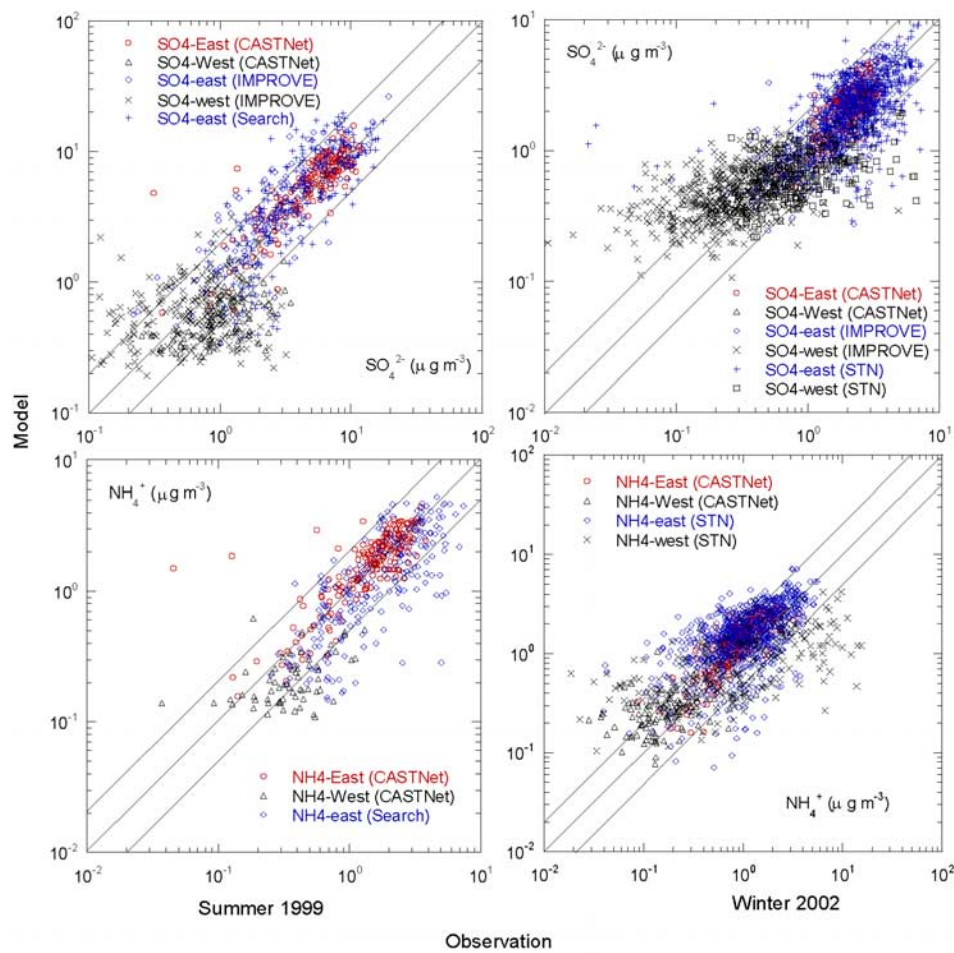
Figure 9. Comparisons of the results of CMAQ model with the observations for aerosol SO_4^{2-} and NH_4^+ for different networks over the United States during 15 June to 17 July 1999 (summer 1999) and 5 January to 18 February 2002 (winter 2002).
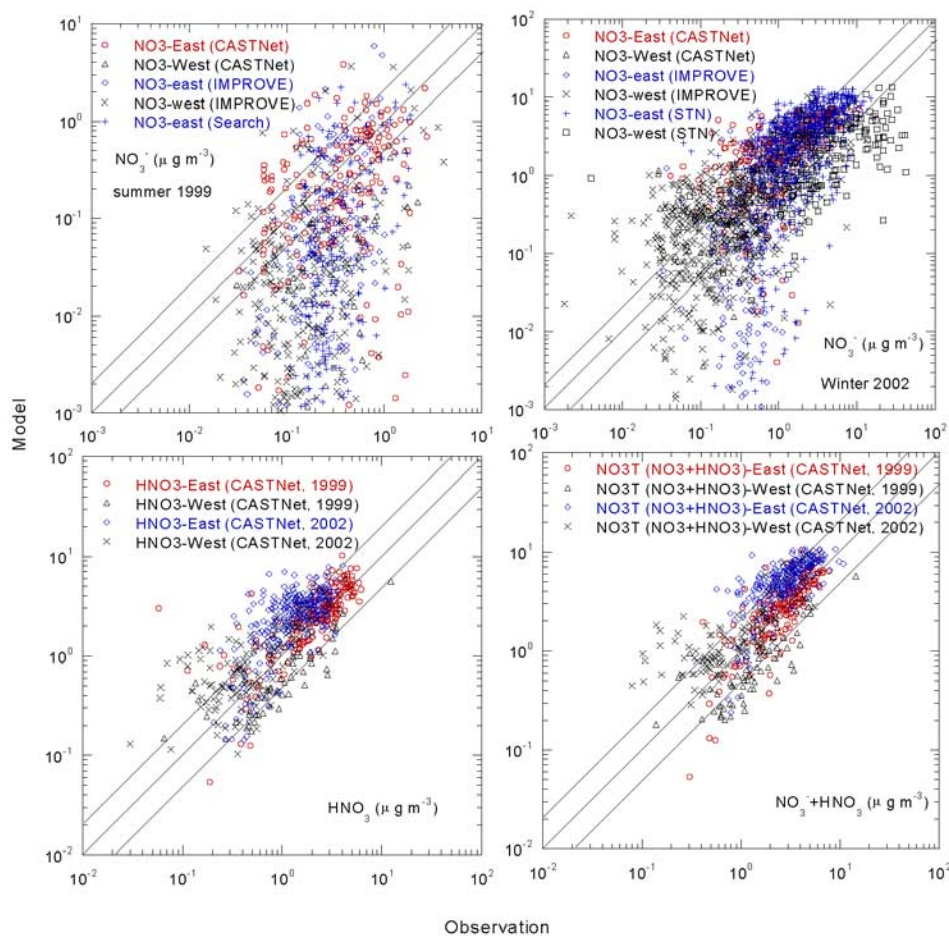
Figure 10. Same as Figure 6 but for aerosol NO_3^-, gas HNO_3, and total nitrate (i.e., aerosol NO_3^- + HNO_3).